

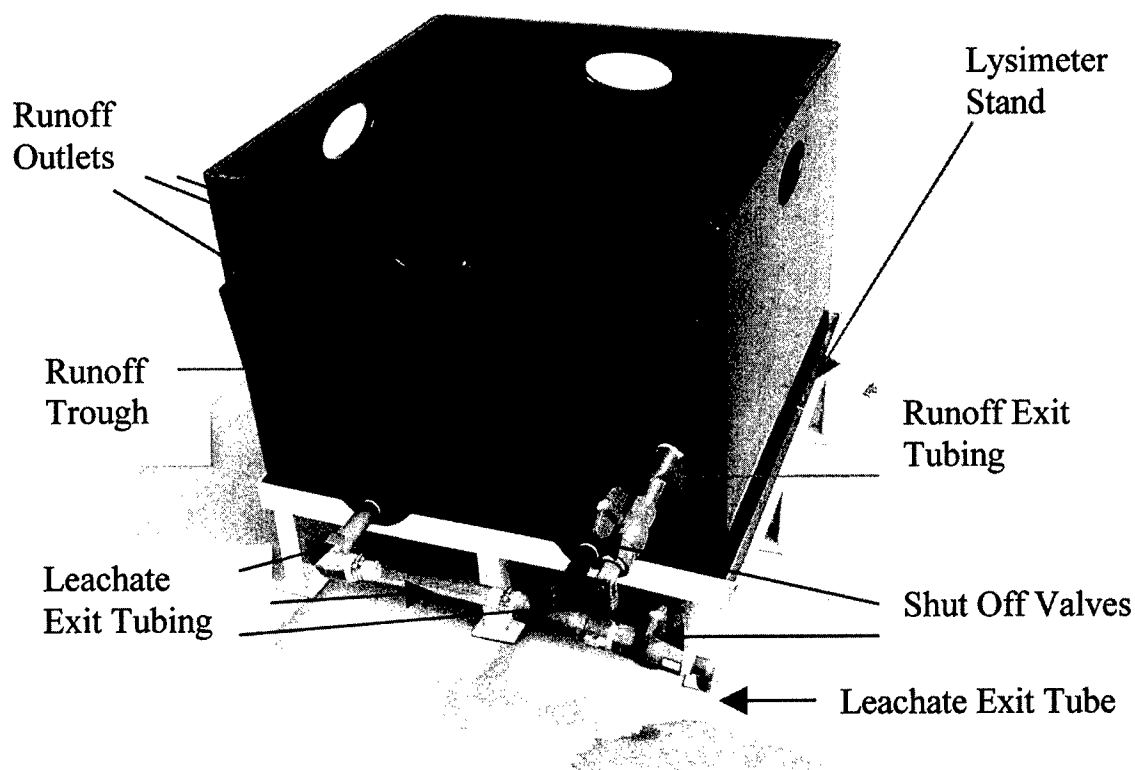


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Topical Application of Phosphate Amendments to Lead-Contaminated Small Arms Firing Range Soils

Steven Larson, Barbara Tardy, Milton Beverly, Allison
Hearn, Michelle Thompson, and Genoa Williams

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and Genoa Williams

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Final report

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ABSTRACT:

Because of the need for lead containment within small arms firing range (SAFR) impact areas, phosphate amendment has been proposed to reduce the release of lead via the surface and groundwater pathway. Both field and laboratory studies have evaluated the use of phosphates to stabilize lead in SAFR soils. The main goal of these studies was to determine the effectiveness of in situ phosphate treatment by demonstrating that phosphate addition to lead-contaminated soils resulted in soils that were stable to lead-leaching as measured by various standards. Because these studies were conducted using either large- or small-scale field demonstration projects or static laboratory procedures that were not capable of simulating conditions on actual ranges, their predictive value is limited. Prior to expending operational funds for large-scale soil amendment projects, further evaluation of the effectiveness of lead containment using phosphate amendment in a more realistic system is needed.

This study evaluated the performance of two phosphate amendments in a more open dynamic system that simulated field conditions at SAFRs. The results of previous laboratory studies were extended by measuring and comparing losses of both soluble and insoluble lead in leachate and runoff from a treated and untreated SAFR soil using specially designed berm lysimeters. A rainfall simulation technique with the capability of increasing rainfall intensity and varying rainfall duration was developed to evaluate lead migration pathways at SAFRs.

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Preface

This report describes the evaluation of in situ stabilization of lead in Small Arms Firing Range (SAFR) soil using two phosphate compounds. The study was conducted with large-scale environmental systems that mimicked field conditions at SAFRs by the Environmental Laboratory (EL), Vicksburg, MS, U.S. Army Engineer Research and Development Center (ERDC), under the Environmental Quality Technology Program, Inorganics in Soils Focus area. Dr. M. John Cullinane, Jr., EL was the Program Manager and Dr. Steve Larson was the Project Manager.

This report was prepared by Dr. Steve Larson and Ms. Barbara Tardy, Environmental Engineering Branch, Environmental Processes and Engineering Division (EPED), and reviewed by Dr. Larry Jones, OA Systems Corporation, Tucson, AZ. Mr. Milton Beverly, Ms. Allison Hearn, Ms. Michelle Thompson, and Mr. Genoa Williams, EPED student contractors, contributed to the report. Dr. Robert M. Engler, Senior Scientist, Dr. Tommy Myers, and Mr. Roy Wade, all of EL, provided in-house technical review of this report.

This study was conducted under the direct supervision of Dr. Patrick Deliman, Chief, Environmental Restoration Branch, and under the general supervision of Dr. Richard E. Price, Chief, EPED, and Dr. Elizabeth C. Fleming, Acting Director, EL.

At the time of publication of this report, Dr. James R. Houston was Director of ERDC, and COL James R. Rowan, EN, was Commander and Executive Director.

1 Introduction

Background

Lead, a highly toxic metal, is the most prevalent contaminant at Superfund sites across the country (U.S. Environmental Protection Agency (USEPA) 2001a). Its presence triggers more Superfund cleanups than any other industrial chemical or waste product. In addition, lead is considered as the number one environmental threat to children's health by the federal government; at very low levels, it is linked to subtle developmental delays and reduced mental function in children (USEPA 2001b, 2003).

Small arms ammunition is made up largely of metallic lead with smaller amounts of alloying materials such as antimony, a hardening agent, and copper and zinc, the primary components in shell casings and jackets. The United States Environmental Protection Agency (USEPA) estimates that 4 percent of the 2 million tons of all lead produced in the U.S. in the late 1990s was made into bullets or shot (USEPA 2001c). Much of this 160 million pounds of lead finds its way into the environment at firing ranges.

Military training and readiness require that most U.S. military installations have and maintain Small Arms Firing Ranges (SAFRs). The U.S. Department of Defense (DoD) oversees more than 3,000 active SAFRs and currently is overseeing the closure or pending closure of more than 200 SAFR sites (Interstate Technology and Regulatory Council (IRTC) 2003).

In addition to these facilities, it is estimated that 9,000 non-military outdoor ranges are now active in the U.S. Private firing ranges enjoy immunity from the environmental laws despite the fact that their operations often result in contamination many times the levels that would trigger major remediation efforts at industrial and military sites (Houlihan and Wiles 2002).

Long-term use of SAFRs results in serious lead contamination from spent ammunition in and around the target berms. Metals are found both as discrete particles ranging from intact bullets or shot to bullet fragments, and as metal complexes in the soil matrix. Typically, more than 96 percent of the lead is present as intact or fragmented bullets or shot (IRTC 2003). Lead bullets striking an impact berm at high speed may vitrify on impact forming "melts" on individual soil particles. Several investigators have demonstrated that lead ammunition exposed to the elements in surface soil will eventually oxidize to an ionic and more soluble form (Manninen and Tanskanen 1993, Lin et al. 1995, Murray et al.

1997). This spent ammunition serves as a source of lead that will contaminate the environment for many years.

Lead contamination can escape from SAFR sites through the air or by the action of rainwater. Small lead particles or “smeared” soil particles may become airborne if wind, foot traffic, or maintenance activities disturb the contaminated soil. Stormwater runoff may erode the lead-contaminated berms and carry the lead and contaminated soil particles away from the SAFR into the local environment. Rainfall intensity, ground slope, and soil type influence the potential transport of lead away from the SAFR. In addition, rainwater, which is typically slightly acidic from the dissolution of carbon dioxide in the air, can dissolve significant amounts of lead and transport it to nearby ground or surface waters. The USEPA has established a Maximum Contamination Level Goal (MCLG) for lead in drinking water of 0 mg/L and has set the action level as required by the Safe Drinking Water Act (SDWA) at 0.015 mg/L; dissolved lead concentrations above 0.015 mg/L are considered a potential health concern (USEPA 2002). The threshold toxicity characterization concentration for lead in contaminated soils established by the Toxicity Characteristic Leachate Procedure (TCLP) is 5.0 mg/L. The universal treatment standard (UTS) for lead is 0.75 mg/L (ITRC 2003).

Currently, the first action in the remediation of a SAFR berm usually entails passing the contaminated soil through a mechanical number 10 sieve to remove debris, rocks, and larger bullet fragments. The remaining soil may be processed through a soil washing treatment train to isolate the finer, enriched fraction. This fraction may then be recycled, disposed, or solidified/stabilized in asphalt emulsion or cement to prevent metal leaching, and the material may then be used in construction projects (Air Force Center for Environmental Excellence (AFCEE) 1998). These techniques were discussed as remediation alternatives at the June 2003 USEPA/IRTC-sponsored conference entitled “Characterization and Remediation of Soils at Small Arms Firing Ranges” (IRTC 2003).

Lead is an amphoteric metal that has its greatest solubility in both acidic ($\text{pH} < 4$) and alkaline ($\text{pH} > 11$) solutions. Under acidic conditions, elemental lead will dissolve releasing a hydrated cation, Pb^{2+} ; under alkaline conditions, elemental lead will dissolve under most circumstances to form the dissolved hydroxide complex $\text{Pb}(\text{OH})_3^-$. When lead exists in a dissolved state, it can sorb to negatively charged clay particle surfaces so that environmental transport can be either attenuated or increased depending upon the mobility of the clay particles.

Several factors will affect the amount of lead that is dissolved in water. In a typical water body, dissolved lead forms precipitates of lead hydroxide [$\text{Pb}(\text{OH})_2$], lead carbonate [PbCO_3 , cerussite], or basic lead carbonate [$\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$, hydrocerussite]. The overall lead solubility in a natural system is fundamentally determined by the concentrations of the anions in solution, e.g., the hydroxide and carbonate ions, and by the ionic strength of the solution which affects the activity coefficients of the ions. These factors can be related to more directly measured parameters such as pH, alkalinity, and total dissolved solids (TDS) (Vaccari 1992). At pH 7, with an alkalinity of 100 mg CaCO_3/L and TDS of 100 mg/L, the theoretical solubility of lead is 0.242 mg/L. At pH 3.5 under these same conditions, the theoretical solubility of lead is 72.6 mg/L.

In any system having water in equilibrium with a solid phase, the metal precipitate that has the lowest solubility will be the only stable solid phase and will increase in its relative concentration at the expense of the more soluble forms. Thus the presence of lead compounds with extremely low solubilities such as lead phosphates influences the solubility and availability of the lead to the environment.

Several laboratory and bench-scale studies have demonstrated the effectiveness of the addition of low levels of phosphate amendments in producing highly insoluble phosphate minerals such as pyromorphite and hydroxypyromorphite (Ma and Rao 1997, Berti and Cunningham 1997, Lambert et al. 1997, Traina and Laperche 1999, Lower et al. 1998). The production of these highly insoluble and stable lead phosphate minerals stabilized the lead so that, even though still present in the soil, the lead in the minerals was not lost in acid leaching tests (Tardy et al. 2003), nor was it bioavailable to soil organisms (Berti and Cunningham 1997, Traina and Laperche 1999, Pearson et al. 2000). The USEPA has recognized that bioavailability of lead in contaminated soils varies greatly depending upon its form in the soil and has suggested that phosphate treatment has potential for in situ remediation of contaminated soils and sediments (USEPA 2001d).

Many of these studies testing the ability of phosphate amendments to stabilize lead in contaminated soils were conducted under small-scale, static laboratory conditions. A major goal of this study was to focus on the application of phosphate amendments to SAFR soils under controlled large-scale, dynamic conditions that mimic field conditions at SAFRs. Special lysimeters were constructed for the application of simulated rainfall to large volumes of treated and untreated soils. They were designed to accommodate the collection of the leachates passing through the soil mass as well as the runoff from the surface of the soil mass. Measured rainfall was applied to the soil mass in weekly applications over a 4-month (16-week) period. The soil mass was then allowed to sit undisturbed for 1 month. Afterward, rainfall was again applied an additional 28 weeks for a total of 44 weeks.

The contaminated soil selected for the study was collected at the former Hamilton Air Force Base (HAFB) in Marin County, California. The base was active from 1932 until 1974 when it was decommissioned. At that time the airfield was transferred to the Army and the housing facilities to the Navy. In 1988, Base Realignment and Closure (BRAC) closed the Army airfield. As a consequence of the BRAC 1993 closure of the Navy's San Francisco bases, the Navy vacated its Hamilton housing in 1996.

Objectives

The specific objectives of the study were as follows:

- Evaluate the long-term effectiveness of two phosphate amendments in reducing the lead mobility in a lead-contaminated SAFR soil under simulated field conditions.

- Assess the resultant loss or release of lead from the SAFR soil into runoff and leachate produced under conditions that simulate natural rainfall.
- Differentiate between lead released from SAFR soil in dissolved form and particulate lead losses.
- Evaluate the effectiveness of the treatment methodology for field-scale application for reduction of lead migration from small arms firing range soil.
- Quantify the mass of phosphate leaving the treated soil.

2 Methods and Materials

Two phosphate amendments found to be the most effective and cost efficient from earlier bench-scale tests were selected for the study (Tardy et al. 2003). The amendments selected, potassium dihydrogen phosphate (potassium phosphate monobasic, KHP) and hydroxyapatite (HAP) powders, were mixed with lead-contaminated SAFR soil at 1- and 5-percent weight/weight, (w/w) levels on a dry weight basis. Two HAFB lead-contaminated soils (8,000 mg/Kg and 80 mg/Kg) were used in the study. The untreated soils were the control soils.

Soil Collection and Preparation

The soils collected from HAFB were transported to the Engineer Research and Development Center (ERDC) in 55-gal, polyethylene-lined drums. A composite sample of the contents of the drums was made by placing each soil on a polyethylene lining in a large concrete area at a depth of about 2 ft. After mixing and tilling with a rotary tiller, six subsamples of each soil were taken for later analysis for lead content. The soil was then stored in 55-gal drums.

Before placement in the lysimeters, several barrels of the raw soil were placed in a large polyethylene pan and mixed again to produce a more homogeneous soil sample. The mixed soil was then placed in a hammer mill crusher for 20 min, then screened through an 8-mesh sieve into a large polyethylene pan and mixed again. The fraction passing the sieve was used in all tests. Samples of the soil were submitted to a complete characterization including soil pH, grain-size distribution, total organic carbon (TOC), cation exchange capacity (CEC), and contaminant concentrations. Although the mixing procedure changed the texture of the soil, this process was necessary in order to produce a more homogeneous soil sample for each lysimeter. Notwithstanding the mixing factor, all tests were conducted in conjunction with the control samples and under the same conditions in order to obtain comparative results.

Design of Large-Scale Lysimeters

Berm dimensions and resulting slopes vary at SAFRs. A cross section of the berm lysimeters designed for this study is illustrated in Figure 1. The lysimeters were made from three-fourths-inch thick, high-density polyethylene and measured 31" by 31" by 24" (inside length × width × height). The lysimeters were

placed on stands constructed from angle iron that were designed with a 0.0625 slope for collection of surface runoff water.

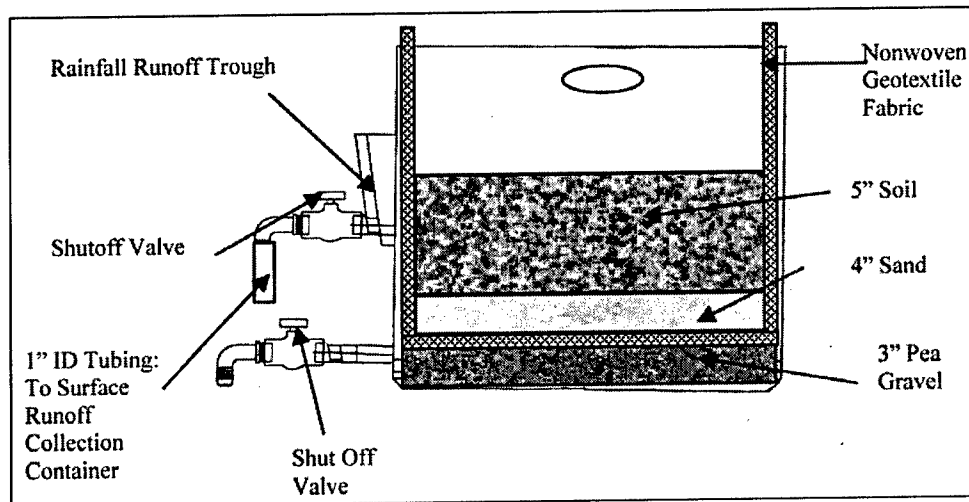


Figure 1. Cross section of lysimeter

Surface Runoff and Leachate Collection System

The lysimeters were designed to allow for the collection of leachate flowing through the soil as well as runoff from the soil surface (Figures 2 and 3). Sufficient room remained above the soil mixture for a portion of the simulated rain to puddle and flow through the runoff trough into the runoff collection system. Leachate and runoff waters were collected in polyethylene pans. All tubing in the collection system was made from non-reactive silicon or polyethylene.

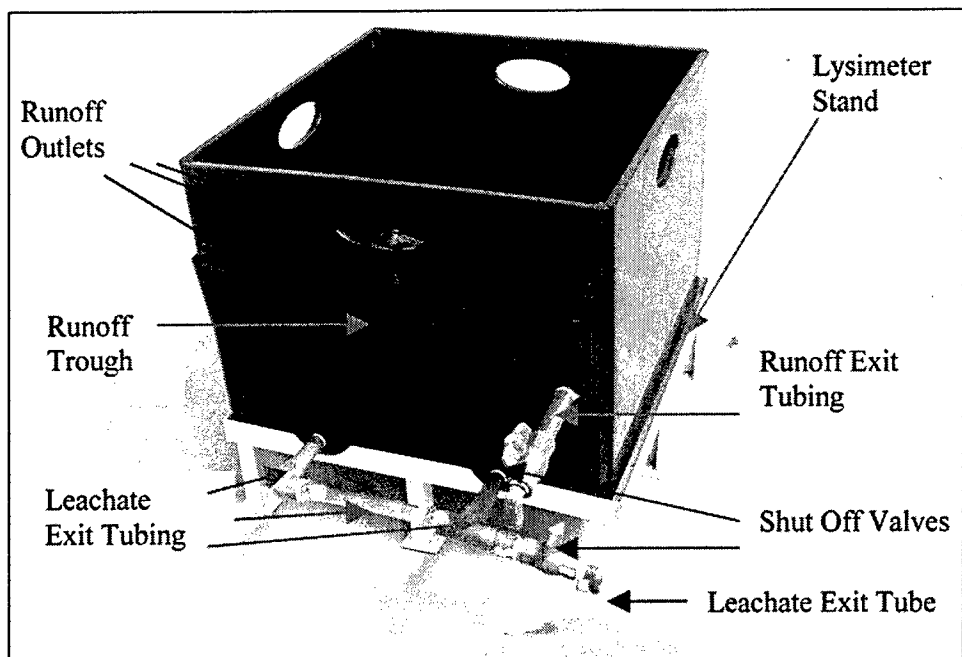


Figure 2. Empty lysimeter cell showing runoff and leachate collection systems

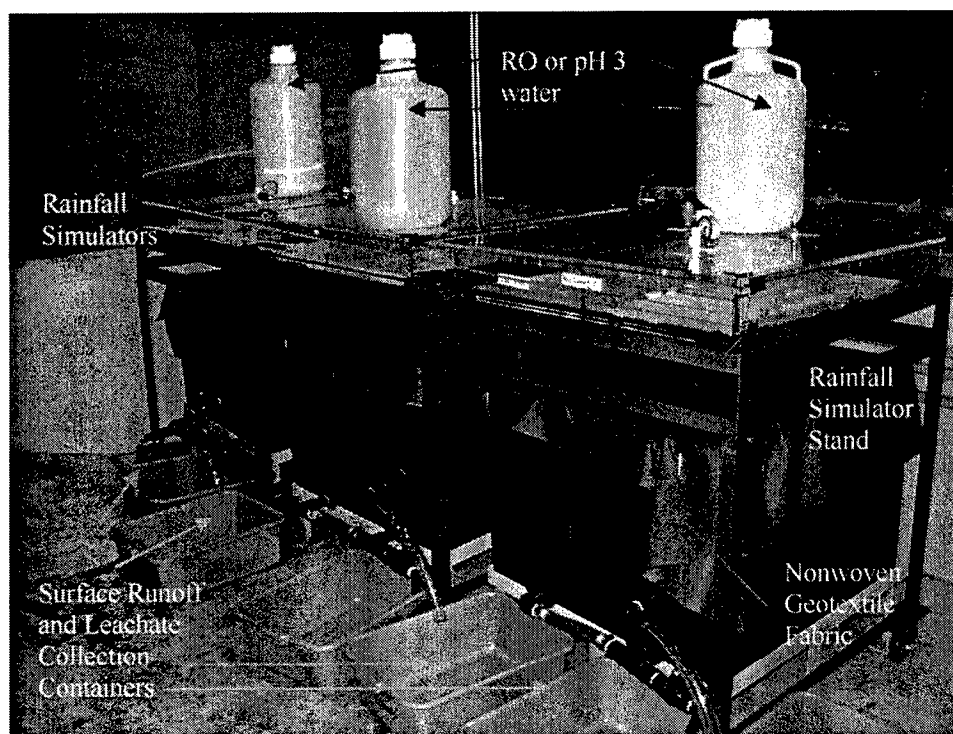


Figure 3. Lysimeters showing rainfall simulators and leachate/runoff collection systems

Simulated Rainfall

The artificial rainwater was introduced through a rainfall simulator made from a clear Plexiglas box that rested on mobile carts directly above the top of the lysimeters (Figure 3). Air pressure regulators were fitted into the top of the simulators to control and vary airflow. The rainfall simulator was designed to apply very low air pressure to increase rainfall rates. A porous polyethylene material was glued to the bottom of the Plexiglas box using silicone adhesive caulk. A water reservoir containing either reverse osmosis (RO) water (neutral pH) or pH 3 RO water was placed on top of the simulator box to supply a measured amount of the appropriate leaching fluid (rainwater) into the box. The fluid flowed through the porous bottom of the rainfall simulator onto the test soil. Approximately 26 min were required to apply the total amount of rainwater.

Simulated rainfall (329 L) over a 16-week period was applied to each lysimeter to replicate a total average annual rainfall of 21 in. (typical in areas near or in Marion County, CA). Eighteen and three-tenths liters (18.3 L) of rainwater was applied over the first 12-week testing period. In order to complete the tests in a timely manner, 27.46 L was added during the last 4 weeks of the experiment. The average weekly application rate was 20.6 L/week (1.31 in./week).

Lysimeter Loading Procedures

The total volume of homogenized, sieved soil was divided into 10 subsamples to provide on average a soil mass of 109 Kg for the lysimeters. Soil subsamples for each lysimeter were weighed and mixed in a rotary cement mixer for 15 min with the appropriate amount of amendment.

Three inches of pea gravel were placed on the bottom of the lysimeter to prevent the sediment from clogging the exit tubes and to collect any accumulated leachate during the weekly rainfall event. A layer of non-woven geotextile was placed on the pea gravel and draped around the inside of the lysimeter. A 4-in. layer of coarse sand was placed on the geotextile, and the sand was compacted to 3 in. On average, 109 Kg of the SAFR soil mixture was then placed in three, 3-in. increments over the sand layer and was compacted to form a soil layer approximately 5 in. deep. Photographs of loaded lysimeters are shown in Figures 4 and 5.

Prior to conducting the tests, the lysimeter cells were saturated with RO water supplied from a 60-L polyethylene bottle. One end of a long piece of silicone tubing was attached to the dispensing outlet of the bottle, and the opposite end was connected to the leachate exit tube at the bottom of each lysimeter. Silicone tubing attached to an air pressure pump was fitted with a female quick-connect valve. A male quick-connect valve was placed in a large one-holed silicone stopper, and the stopper was placed in the top of the bottle. The bottle was then placed on a tall mobile stand and positioned over each lysimeter. Approximately 45 L of pressurized water was allowed to drain into each lysimeter in an upward mode through all layers. After complete saturation occurred as evidenced

by a water layer on top of the soil mass, excess water was drained from each lysimeter.

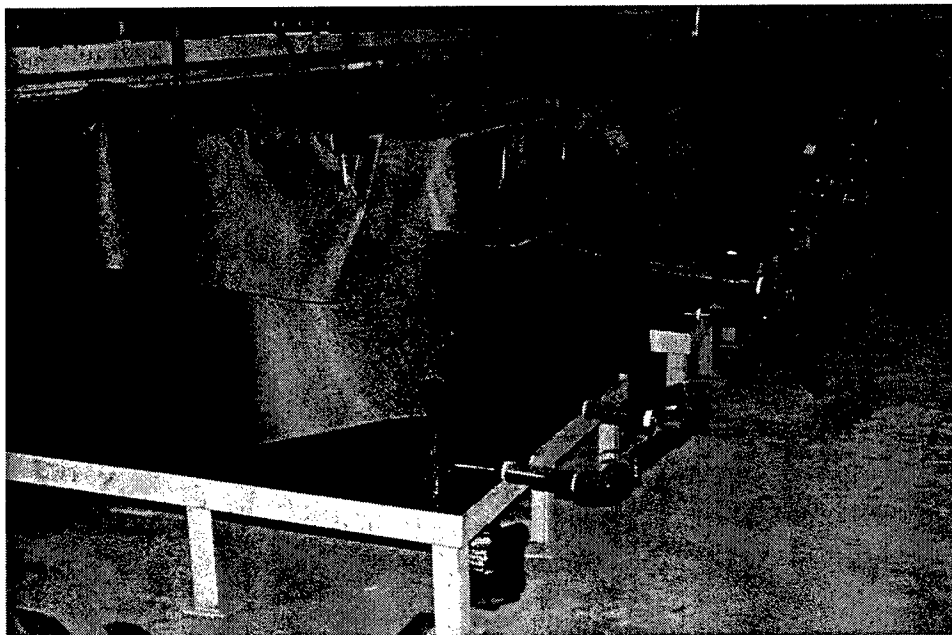


Figure 4. Set of loaded lysimeters

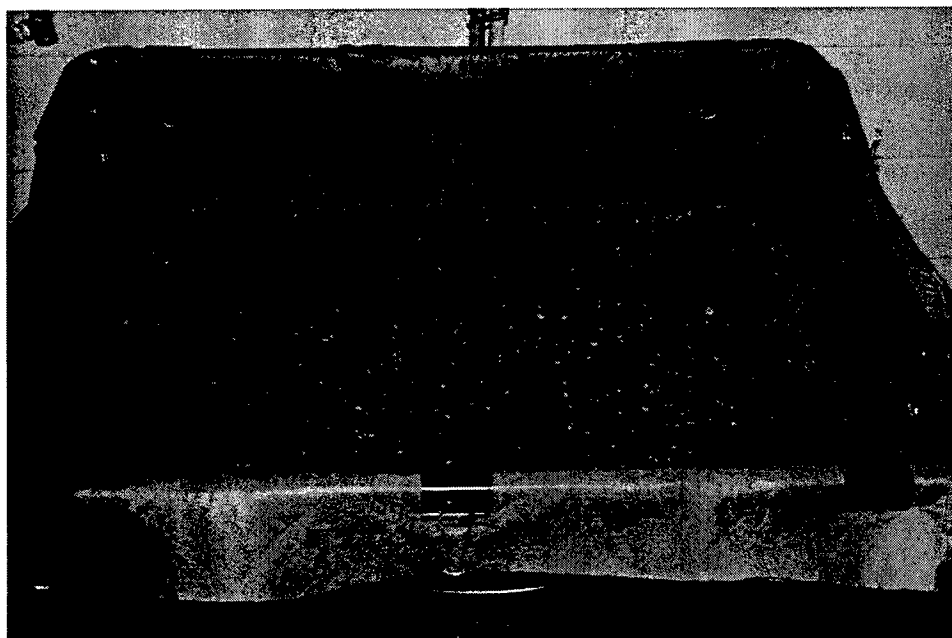


Figure 5. Loaded lysimeter showing soil surface

Experimental Design

Ten lysimeters loaded with 8,000 mg/kg lead-contaminated HAFB soil were used in the rain simulation study: two lysimeters were controls with no

amendment added; two sets of four lysimeters each were treated with 1- and 5-percent w/w of the two phosphate amendments (potassium dihydrogen phosphate and hydroxyapatite). On a weekly basis, artificial rainwater (RO water) at a neutral pH was supplied to one set of five lysimeters; artificial rainwater at pH 3 (RO water adjusted to pH 3 with nitric acid) was supplied to the other set. The lysimeters were left uncovered after each weekly rain event. The experimental design including the contents of each of the lysimeters and their associated leaching fluids is diagramed in Figure 6, and the loading of the lysimeters is shown in Table 1.

HAMILTON AFB pH \approx 7 Rainwater Control Sample 0% Treatment CELL #1	HAMILTON AFB pH \approx 7 Rainwater 1% Potassium dihydrogen phosphate $\text{KH}_2(\text{PO}_4)$ KHP CELL #2	HAMILTON AFB pH \approx 7 Rainwater 5% Potassium dihydrogen phosphate $\text{KH}_2(\text{PO}_4)$ KHP CELL #3	HAMILTON AFB pH \approx 7 Rainwater 1% Hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ HAP CELL #4	HAMILTON AFB pH \approx 7 Rainwater 5% Hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ HAP CELL #5
HAMILTON AFB pH \approx 3 Rainwater Control Sample 0% Treatment CELL #6	HAMILTON AFB pH \approx 3 Rainwater 1% Potassium dihydrogen phosphate $\text{KH}_2(\text{PO}_4)$ KHP CELL #7	HAMILTON AFB pH \approx 3 Rainwater 5% Potassium dihydrogen phosphate $\text{KH}_2(\text{PO}_4)$ KHP CELL #8	HAMILTON AFB pH \approx 3 Rainwater 1% Hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ HAP CELL #9	HAMILTON AFB pH \approx 3 Rainwater 5% Hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ HAP CELL #10

Figure 6. Experimental design showing cell contents, leaching fluid pH, and lysimeter nomenclature

TCLP extractions were performed on the treated and untreated 8,000 mg/kg lead-contaminated HAFB soil before and after rain simulation tests were conducted. For comparative purposes only, TCLP extractions were also carried out on an HAFB 80 mg/L lead soil. Rain simulation tests were not conducted on the 80 mg/kg soil. The TCLP was conducted on the two soils before amendment addition and immediately following amendment with 1 and 5 percent HAP and KHP. This evaluation of the characteristic leaching properties of the soils was done in order to further assess the effects of the phosphate additives on lead losses from soils containing a low and high level of lead.

Table 1 Lysimeter Soil Additive, Loading, and pH of Simulated Rain				
Lysimeter Number	Phosphate additive	Amount of additive (% w/w)	Total soil mixture added (Kg dry wt)	Artificial rainwater pH
Cell 1	None Control	0	128.3	7
Cell 2	Potassium dihydrogen phosphate	1	108	7
Cell 3	Potassium dihydrogen phosphate	5	108	7
Cell 4	Hydroxyapatite	1	108	7
Cell 5	Hydroxyapatite	5	108	7
Cell 6	None Control	0	108	3
Cell 7	Potassium dihydrogen Phosphate	1	97.95	3
Cell 8	Potassium dihydrogen Phosphate	5	108	3
Cell 9	Hydroxyapatite	1	108	3
Cell 10	Hydroxyapatite	5	108	3

Physical and Chemical Analysis

The physical characteristics of the SAFR soil were determined by standard laboratory procedures. Specific gravity, particle-size distribution, and soil classification were determined according to the American Society for Testing and Materials (ASTM 2001) procedures D-854, D-422, and D-2487, respectively. Chemical analyses were performed according to the standard analytical methods listed in Table 2. Chemical characterization of the SAFR soil included lead content and lead quantities after TCLP testing, TOC, CEC, pH, aqueous phosphate concentration, and total suspended solids (TSS).

The initial lead content of the SAFR soil was determined after the soil sample was digested according to SW-846 Method 3051 (USEPA 1999). Leachate and runoff samples were analyzed for dissolved lead, total lead, TCLP lead, TSS, and phosphate. Aqueous leachate and runoff samples were analyzed for dissolved lead after filtering through a 0.45-micron filter following the procedures in Method 3010 (American Public Health Association 1998). Total (digested) lead was determined on liquid samples (leachates and runoff) after digestion procedures according to SW-846 Method 3015. All TCLP, leachate, and runoff samples containing greater than 1 mg/L lead were analyzed for lead content by SW-846 Method 7420 (USEPA 1999) Flame Atomic Absorption Spectroscopy using a Perkins Elmer 5100 Flame Atomic Absorption Spectrophotometer. Lead quantification for samples containing less than 1 mg/L lead was according to EPA SW846 Method 6010B Inductively Coupled Plasma (USEPA 1999) on a Perkins Elmer Optima 3000 or by SW846 Method 6020 Inductively Coupled Plasma-Mass Spectrometry (USEPA 1999) on a Perkins Elmer Sciex 6000. TOC and CEC were measured on a Zellweger Astro Lab TOC Analyzer Model 2100 and a Thermal Jarrell Ash Model 61E, respectively. Phosphate levels were

determined on filtered samples and were measured on a Dionex Ion Chromatograph Model CD 20.

Each analytical run included triplicate distilled-deionized (DDI), triplicate RO water blanks, and triplicate QC reagent standards. The percent standard deviation of the reagent QC standards was typically less than 5 percent. Blank values were subtracted from the measured values.

Table 2
Chemical Analytical Methods

Parameter	Method	Detection Limit	
		Water (mg/L)	Soil (mg/Kg)
Lead TCLP lead	SW-846-7420 ¹ SW-846-6020 ¹ SW-846-1311 ¹	1 <0.00002	1 <0.00002
Phosphate	SW-846-9056 ¹	0.1	0.1
TOC	SW-846-9060 ¹	0.05	0.5
CEC	SW-846-9081	ND ³	ND
pH	SW-846-9045C	NA ⁴	NA
TSS	Standard Method 2540D ²	NA	NA

¹ U.S. Environmental Protection Agency (USEPA 1999).

² American Public Health Association 1998.

³ ND = No data provided

⁴ NA = Not Applicable

3 Results and Discussion

HAFB Soil Characterization

The initial properties of the HAFB soil are summarized in Table 3. According to ASTM procedure D-2487 (ASTM 2001), the SAFR soil classifies as a sandy clay with 19.1 percent sand and 80.3 percent fines. The grain-size distribution of the soil and the coarse sand layer are charted in Appendix A (Figures A1 and A2). The level of TOC found in the soil (about 1.7 percent) indicates a moderate amount of organic material. A CEC of 28-meq/100 g is typical of a dark-colored loam, a silty clay loam, or a silty clay.

The replicate analyses of the lead content of the first composite soil and the final milled and mixed soil samples are presented in Tables A1 and A2 in Appendix A. Lead results from the initial composite soil were variable and often had standard deviation values higher than the average lead concentration values. The overall average of 18 analyses was 31,680 mg/kg with a 132 percent relative standard deviation. The soil loaded in the lysimeters showed less variability and averaged 8,100 mg/kg lead with a 21 percent relative standard deviation, indicating that the high variability of the initial composite soil was lowered significantly after further processing and mixing.

Table 3
HAFB Soil and Sand Properties

Property	Soil	Coarse Sand
Specific gravity	2.73	2.65
Percent fines	80.3	2.6
Percent sand	19.1	97.4
Unified soil classification	CL	SP
Lead content	8,100 mg/Kg	ND ¹
TOC	17,000 mg/Kg	ND
CEC	28 meq/100 g	ND
pH	6.55	7.02
¹ ND = not determined		

Runoff and Leachate Collection

Leachate and runoff samples were collected from the lysimeters during each weekly application of artificial rainfall. The samples were assayed for total volume of leachate and runoff, pH, TSS, phosphate, dissolved lead, and total digestible lead content.

Volumes of leachate and runoff collected

The total amount of leachate and runoff from each of the lysimeters is summarized in Table 4 and graphed in Figure 7. The percentage of total volume collected as leachate or runoff from each lysimeter is shown in Table 5. The volume of effluent collected after each rain event is shown in Tables A4 and A5 in Appendix A.

The average of the total leachate and runoff collected each week was less than the amount added weekly. The difference between the sum of the leachate and runoff volumes and the volume applied each week can be attributed to water absorption by the soil, evaporation, and/or rewetting of less than the saturated soil within the lysimeter.

Although somewhat variable, a distinct pattern does not exist between the ratio of leachate to runoff volume and the high and low pH cells or the amount and type of additives in the cells. This finding suggests that neither pH nor additive type greatly affected the hydraulic characteristics of the soil and/or that further testing is required before a definitive conclusion can be reached.

Table 4					
Average Leachate and Runoff Collected from Lysimeters					
Lysimeters with pH 7 leachant					
Cell number and additive	Cell 1 Control	Cell 2 1% KHP	Cell 3 5% KHP	Cell 4 1% HAP	Cell 5 5% HAP
Total Leachate collected (L)	206.0	151.8	135.2	131.0	101.4
Total runoff collected (L)	83.5	130.6	130.1	116.9	168.0
Total leachate & runoff (L)	289.4	282.4	265.2	244.9	269.4
Average leachate & runoff rate (L/week)	18.1	17.6	16.6	15.3	16.8
Lysimeters with pH 3 leachant					
Lysimeter number and additive	Cell 6 Control	Cell 7 1% KHP	Cell 8 5% KHP	Cell 9 1% HAP	Cell 10 5% HAP
Total Leachate collected (L)	142.3	130.6	153.7	114.9	138.6
Total runoff collected (L)	117.4	108.8	91.9	131.8	133.4
Total leachate & runoff (L)	259.7	239.3	245.6	246.7	272.1
Average leachate & runoff rate (L/week)	16.2	15.0	15.3	15.4	17.1

Table 5 Percent of Collected Volume as Leachate or Runoff					
Parameter	Percent of effluent volume				
Lysimeters with pH 7 leachant					
Lysimeter number and additive	C1 Control	C2 1% KHP	C3 5% KHP	C4 1% HAP	C5 5% HAP
% of total, leachate	71	54	51	52	38
% of total, runoff	29	46	49	48	62
Lysimeters with pH 3 leachant					
Lysimeter number and additive	C6 Control	C7 1% KHP	C8 5% KHP	C9 1% HAP	C10 5% HAP
% of total, leachate	55	55	63	47	51
% of total, runoff	45	45	37	53	49

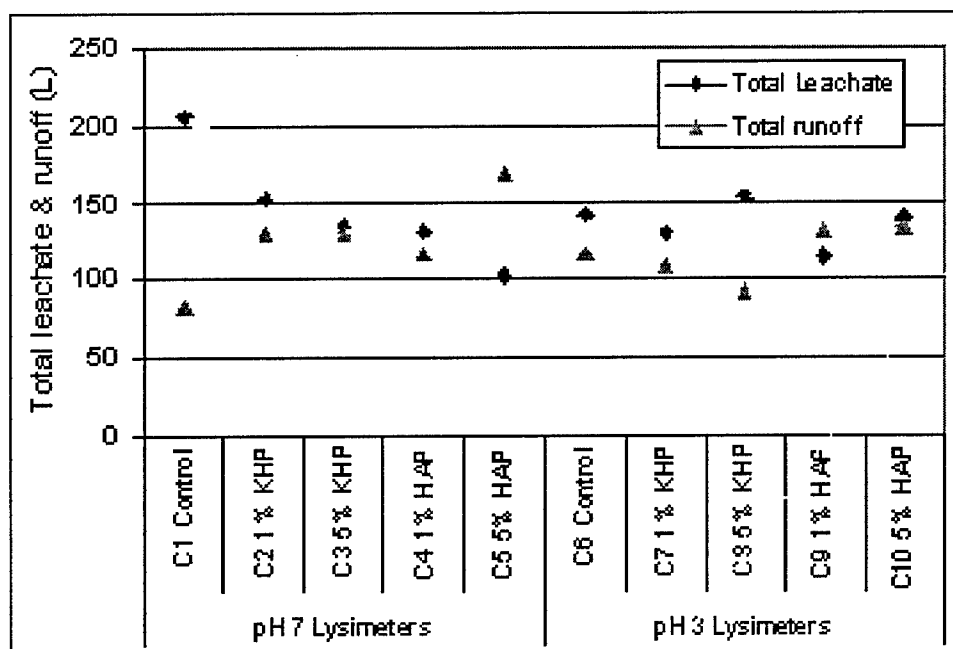


Figure 7. Total amount of leachate and runoff collected for each lysimeter over the 16-week leaching period

Leachate and runoff pH

pH 7. Leaching of the lysimeters with pH 7 rainwater produced leachates in a range slightly below pH 6 and slightly above pH 8 in the cells (Figure 8A). Early leachate pH values in these cells varied between 7 and 8 but declined over the first 9 weeks to values between pH 6 and 7 for the remainder of the experiment. KHP additive at 5 percent had the most effect on the leachate pH values, lowering the pH values over the experiment by around one pH unit. Leachate pH values of the HAP amended soil were similar.

With the exception of one sample, the pH of the runoff samples (Figure 8C) exhibited similar patterns. The lysimeters leached at pH 7 produced very consistent runoff pH values between 6 and slightly above 7 for all cells.

pH 3. Artificial rainwater at pH 3 had a different effect on the leachate pH values (Figure 8B). With one exception (5 percent KHP), the pH values for the first 2 to 3 weeks were similar to the pH 7 leached cells averaging around pH 7 and 8. However, with the exception of 5 percent KHP and HAP, over the remaining experimental period, the more acidic rainwater overcame the buffering capacity of the soil slowly lowering the pH to values between about pH 4.8 and 3.5. At the beginning of the experiment, the leachate pH values from the 5 percent KHP and 5 percent HAP additives measured about 5.3 and 7.5, respectively. The 5 percent KHP additive tended to hold the leachate pH steadily below 6 throughout the pH 3 experiments while the 5 percent HAP treatment held the pH above 6.

The pH of the runoff samples (Figure 8D) exhibited similar patterns over the course of the experiment. Initially, runoff pH values of the control with no additive were lower than runoffs containing KHP and HAP additives. Initial runoff samples collected had pH values measuring between 5 and 7; however, over the length of the experiment, the pH values of the samples including the control were gradually reduced to the value of the rainwater, around pH 3 for the last four sampling periods.

These results indicate that leachate pH is more affected by the amount of additive than by rainfall pH, and, conversely, runoff pH is more affected by the rainfall pH than by the amount of additive. This is to be expected since runoff water washes the soil surface repeatedly and leachate permeates through a larger soil mass and is more affected by the additives.

TSS in Leachates and Runoff

TSS leachate and runoff results are listed in Appendix A (Tables A10 and A11), and the average TSS concentrations are summarized in Table 6. TSS in leachates were generally high in the first few samples and typically declined over the length of the study. Except for some high values in individual early samples, TSS levels in the leachates were consistently below 100 mg/L (Appendix A, Table A10).

At pH 7, with the exception of the 1 percent KHP treatment, both phosphate amendments significantly lowered the average TSS concentrations in the leachates as compared with the control, reducing them by over 80 percent (Table 6). The first 1 percent KHP TSS leachate sample had a high TSS concentration of over 11,000 mg/L. Later samples from this lysimeter were more typical of the other KHP leachates. At pH 3, the opposite effect was noted. In comparison with the control, after phosphate amendment average TSS leachate concentrations in all samples increased.

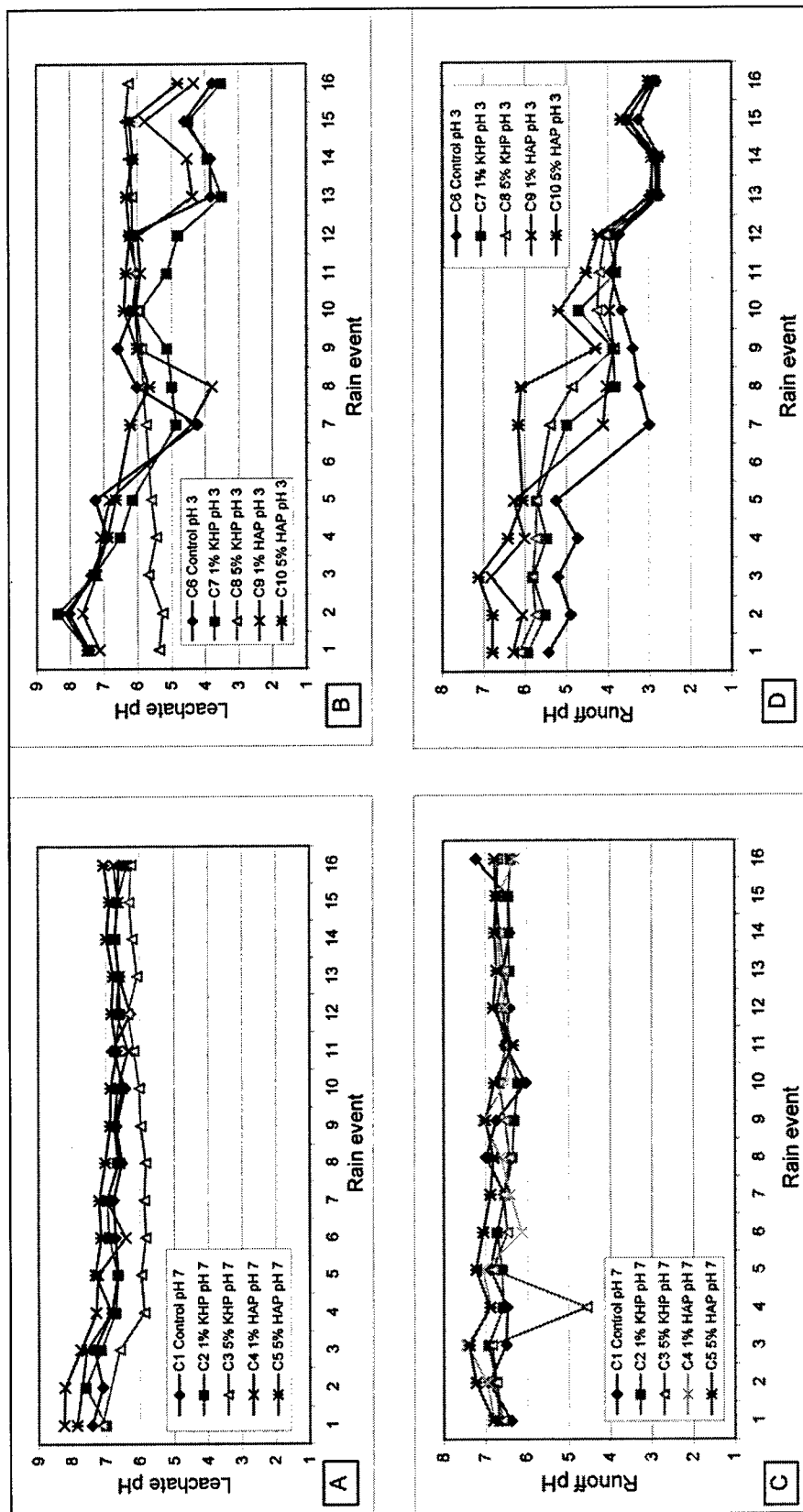


Figure 8. Leachate and runoff pH values after each rain event: (A) Leachate pH for pH 7 lysimeters, (B) Leachate pH for pH 3 lysimeters, (C) Runoff pH for pH 7 lysimeters, (D) Runoff pH for pH 3 lysimeters

With the exception of the 1 and 5 percent KHP at pH 3, TSS average concentrations in the runoff from all lysimeters exceeded the level in the control runoff at both pH values (Table 6).

Figures 9 and 10 show the accumulated TSS in leachates and runoffs. At pH 7 1 percent HAP, 5 percent HAP, and 5 percent KHP lowered the accumulated TSS in leachates, while the 1 percent KHP increased the TSS. At pH 3, both phosphate treatments increased the leachate accumulated TSS in comparison to the control. Accumulated TSS in the runoff from all but one (5 percent KHP at pH 3) of the lysimeters at both pH values increased after phosphate amendment in comparison with the control. The 5 percent KHP runoff at pH 3 showed a decrease in accumulated TSS.

Table 6					
Average TSS Concentration in Leachates					
Parameter	Phosphate additive				
	Control	1% KHP	5% KHP	1% HAP	5% HAP
pH 7 lysimeters					
Lysimeter	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5
Average TSS conc. in leachate ¹ (mg/L)	141	176	25.4	10.4	26.6
Average TSS conc. in runoff (mg/L)	643	1150	954	2,105	748
pH 3 lysimeters					
Lysimeter	Cell 6	Cell 7	Cell 8	Cell 9	Cell 10
Average TSS conc. in leachate (mg/L)	18.7	95.8	96.8	26.9	45.5
Average TSS conc. in runoff (mg/L)	915	859	532	1,321	1,575
¹ Total mg TSS in all leachates or runoff divided by the total volume of leachate or runoff collected					

Effects of Phosphate Additives on Lead Releases in Leachates and Runoff

Dissolved metals are defined in Method 3010 as “those constituents (metals) of an unacidified sample that pass through a 0.45 micrometer membrane filter” and total metals are defined as “the concentration of metals determined on an unfiltered sample after vigorous digestion, or the sum of the concentrations of metals in both dissolved and suspended fractions” (American Public Health Association 1998). The leachate and runoff samples from the lysimeter effluents were analyzed for both dissolved and total lead.

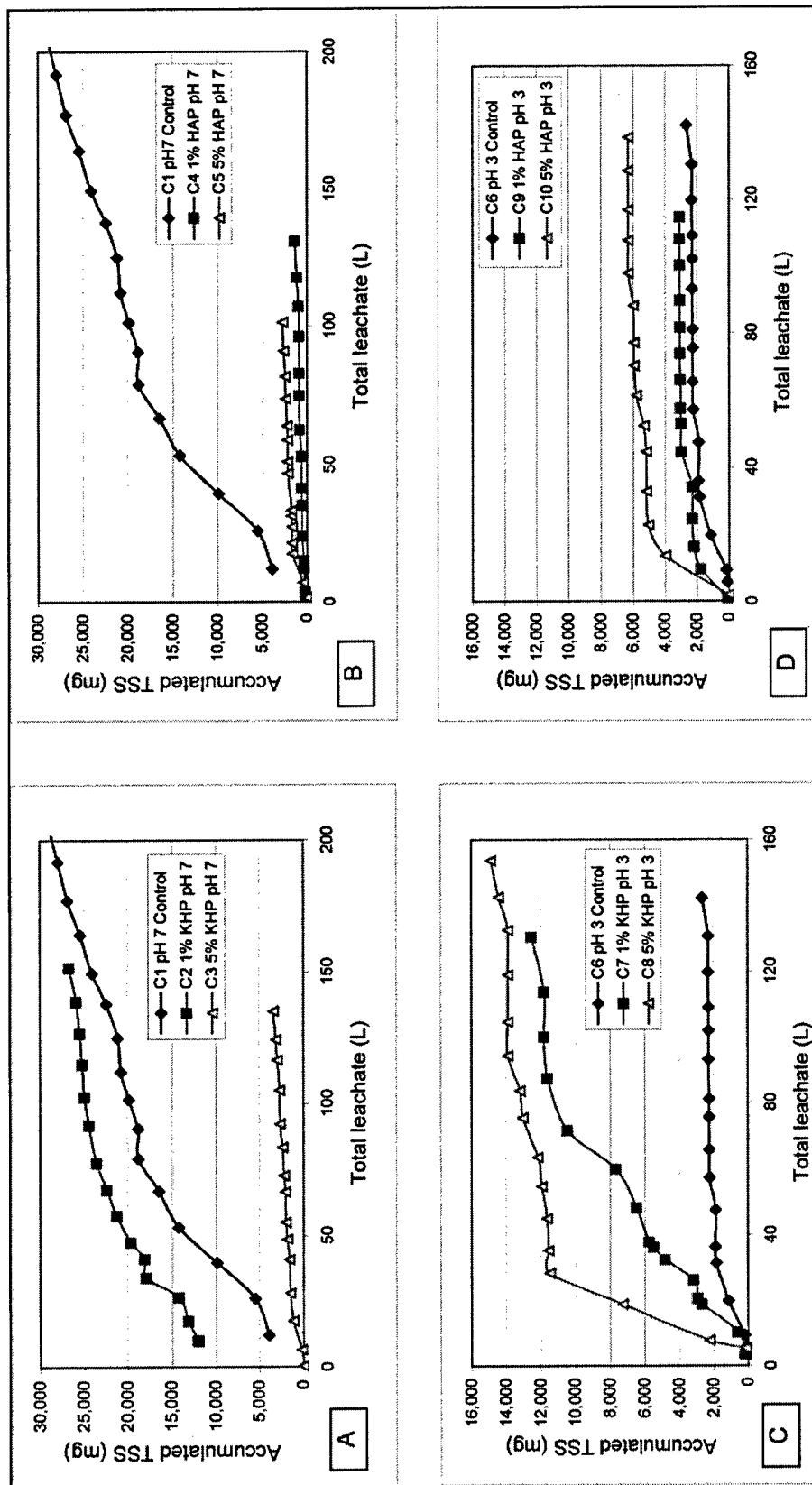


Figure 9. Accumulated total suspended solids (TSS) in leachates: (A) KHP addition at pH 7, (B) HAP addition at pH 7, (C) KHP addition at pH 3, (D) HAP addition at pH 3

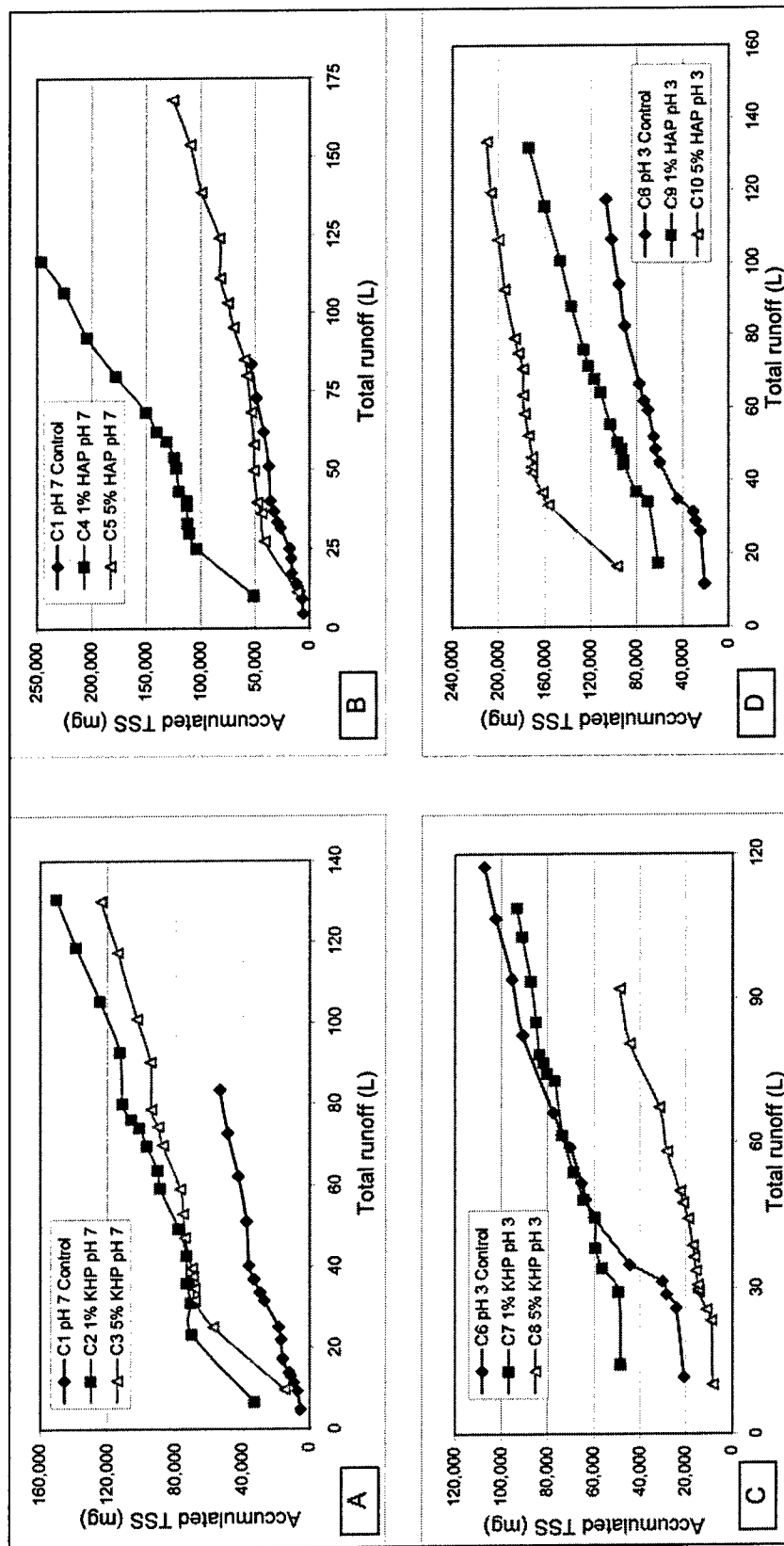


Figure 10. Accumulated total suspended solids (TSS) in runoff: (A) KHP addition at pH 7, (B) HAP addition at pH 7, (C) KHP addition at pH 3, (D) HAP addition at pH 3

Dissolved lead in leachates from lysimeters

pH 7 leachates. The lead concentration results for each leachate sample collected are shown in Appendix A (Table A6). The average and highest lead concentration values and the total mass of lead released are listed in Table 7. The lead results from the phosphate-treated cells are compared with that from their corresponding control cell. The total amount of lead leached from the control lysimeter at pH 7 was 3.9 mg in a total volume of 206 L of leachate, giving an average leachate concentration of 0.019 mg/L (Table 8). The highest concentration found in the control pH 7 leachates was near 0.045 mg/L, above the SDWA standard of 0.015 mg/L. The highest lead concentration from any soil sample was well below the TCLP regulatory level of 5.0 mg/L.

The 1 percent KHP and control leachates were similar in the levels of dissolved lead released, both having an average dissolved lead concentration of about 0.020 mg/L. Five percent KHP in the soil lowered the total dissolved lead level to 0.009 mg/L in comparison to the 0.015 mg/L SDWA standard.

HAP addition decreased the dissolved lead released from 0.019 mg/L to an average concentration of 0.003 mg/L for 1 percent HAP addition and 0.008 mg/L for 5 percent addition, again below the SDWA standard.

The accumulated amounts of dissolved lead in pH 7 leachates are illustrated in Figure 11. In general, as compared with the control cell at the same pH, the accumulated dissolved lead levels were reduced over the course of the experiment with the addition of 5 percent KHP and both 1 and 5 percent HAP. Accumulated lead releases were about the same as the control sample after a 1 percent KHP treatment (Figure 11A).

pH 3 leachates. In order to simulate aggressive weathering of the soils, acid rain was applied to lysimeter numbers 6 through 10. Artificial rainwater at pH 3 increased the level of dissolved lead released from the control soil (Cell 6) by about 27-fold (Table 7). Lead concentrations in all the leachates were below the 5.0-mg/L regulatory level for lead. The highest lead concentration in the control leachate at pH 3 was 2.22 mg/L, and the average value was 0.52 mg/L, both above the SDWA standard.

Both HAP and KHP treatment reduced the release of dissolved lead in the pH 3 leachates, especially at the 5-percent addition level. HAP addition reduced the total mass of lead released by approximately 70 and 98 percent for the 1- and 5-percent additions, respectively. At 1- and 5-percent additions, KHP treatment reduced the lead mass by 65 and 94 percent from the control levels, respectively.

The accumulated mass of lead in the control leachate samples at pH 3 was quite variable, showing very little loss over the first 40 L of leachate and increasing dramatically in the last third of the samples (Figures 11B and 11D). This later increase in lead mass was related to the progressive decrease in pH in the pH 3 leachate samples over the experiment. In comparing pH results (Figures 9B and 9C) to leachable dissolved lead results (Figures 11B and 11C), a strong correlation exists between pH and dissolved lead, implying that to some extent amendments work by controlling pH.

Table 7
Average and Highest Sample Concentrations and Mass of Dissolved Lead in Leachates After 16 Rain Events

Parameter	Phosphate Additive				
	Control	1% KHP	5% KHP	1% HAP	5% HAP
pH 7 lysimeters					
Lysimeter	C1	C2	C3	C4	C5
Average lead conc. in leachate (mg/L) ¹	0.019	0.020	0.009	0.003	0.008
Highest single leachate value (mg/L)	0.045	0.028	0.230	0.009	0.044
Total mass of dissolved lead leached (mg)	3.88	3.09	1.23	0.39	0.77
pH 3 lysimeters					
Lysimeter	C6	C7	C8	C9	C10
Average lead conc. in leachate (mg/L)	0.52	0.180	0.030	0.16	0.009
Highest single leachate value (mg/L)	2.22	0.418	0.072	1.05	0.770
Total mass of dissolved lead leached (mg)	74.3	22.8	4.63	18.5	1.23
¹ Total mg dissolved lead in all leachates divided by the total volume of leachate collected					

Dissolved lead in runoff from lysimeters

pH 7 runoff. The concentration of dissolved lead in each runoff sample after each rain event is shown in Appendix A (Table A8). The mass of lead released and the average and highest lead concentrations are summarized in Table 8. The runoff contained an average dissolved lead concentration of 0.064 mg/L. The highest concentrations (0.284, 0.247, and 0.245 mg/L) in any individual sample (Table 8) were near the theoretical solubility of lead (0.242 mg/L) at pH 7.

Addition of 5 percent HAP lowered the average concentration of dissolved lead in the pH 7 runoff by around 60 percent to a value of 0.021 mg/L. However, at 1 percent, HAP had very little effect on dissolved lead concentration. KHP addition exhibited minimal effect on dissolved lead concentrations in the runoffs at both addition levels. Again, these concentrations were well below the 5-mg/L regulatory level for lead but above the SDWA standard of 0.015 mg/L.

The accumulated amount of dissolved lead in runoff from the lysimeters is shown in Figure 12. The runoff from the control lysimeter contained an overall total of 40 percent more dissolved lead in 60 percent less volume than the corresponding control runoffs. Accumulated dissolved lead in runoff from the 5 percent HAP treatment was lower than the control or the 1 percent HAP, while lead levels from both KHP treatments were higher than the levels in the control. The 5 percent HAP treatment indicates that lead was immobilized (decreased lead mobilization), and the KHP treatments mobilized lead (increased lead mobilization).

Table 8 Average and Highest Concentrations and Mass of Dissolved Lead in Runoff After 16 Rain Events					
Parameter	Phosphate Additive				
	Control	1% KHP	5% KHP	1% HAP	5% HAP
pH 7 lysimeters					
Lysimeter	C1	C2	C3	C4	C5
Average lead conc. in runoff (mg/L) ¹	0.064	0.091	0.091	0.062	0.021
Highest single runoff value (mg/L)	0.284	0.247	0.245	0.121	0.042
Total mass of dissolved lead in runoff (mg)	5.37	11.8	11.9	7.25	3.58
pH 3 lysimeters					
Lysimeter	C6	C7	C8	C9	C10
Average lead conc. in runoff (mg/L)	4.56	0.745	0.453	4.49	0.97
Highest single runoff value (mg/L)	13.5	1.74	0.888	9.76	3.80
Total mass of dissolved lead in runoff (mg)	535	81.0	41.6	592	62.6
¹ Total mg dissolved lead in all runoff divided by the total volume of runoff collected					

pH 3 runoff. The concentration values for dissolved lead in the runoff after each rain event are listed in Appendix A (Table A8). The mass of lead released, the average lead concentrations, and the highest lead concentrations are summarized in Table 8. The average concentration of dissolved lead (4.56 mg/L) in runoff from the control lysimeter leached at pH 3 (Cell 6) was near 70 times that leached at pH 7. The highest average concentration was 13.5 mg/L. KHP addition to the soil lowered the average concentration to 0.745 and 0.453 mg/L at the 1- and 5-percent addition levels, respectively, representing an 84 and 90 percent reduction. The average runoff concentrations for the 1- and 5-percent HAP were 4.49 and 0.97 mg/L, a 2 and 80 percent reduction, respectively.

The total quantity of accumulated dissolved lead released in pH 3 runoff samples is depicted in Figures 12B and 12D. Only small amounts of lead were lost in runoff from any of the lysimeters with pH 3 rainwater until five or six rain events had occurred and over 30 L of runoff had been collected. Afterward, as the pH of the runoff decreased, the release of dissolved lead in the runoff increased significantly in the control and in the 1 percent HAP treated soil. However, as illustrated in Figures 12B and 12C, the other treatments significantly reduced the quantity of accumulated dissolved lead in the runoff when compared with the control. The reductions, as compared with the control, for both KHP treatments and 5 percent HAP addition were much greater than the 1 percent HAP addition, indicating that these treatments tended to immobilize the lead while lead was mobilized in the control and in the 1-percent HAP treatment.

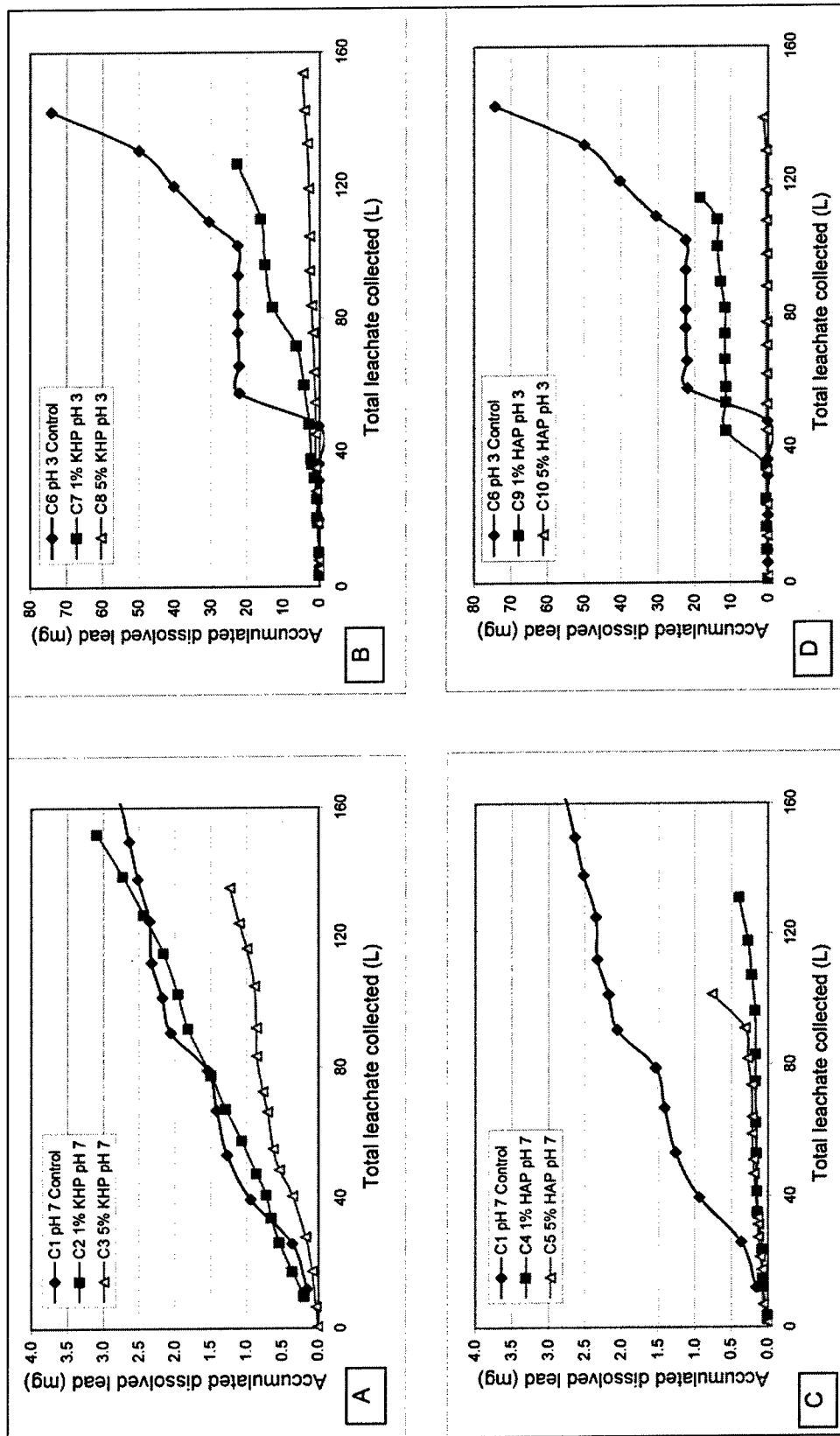


Figure 11. Accumulated dissolved lead in leachates from lysimeters: (A) KHP addition at pH 7, (B) KHP addition at pH 3, (C) HAP addition at pH 7, (D) HAP addition at pH 3

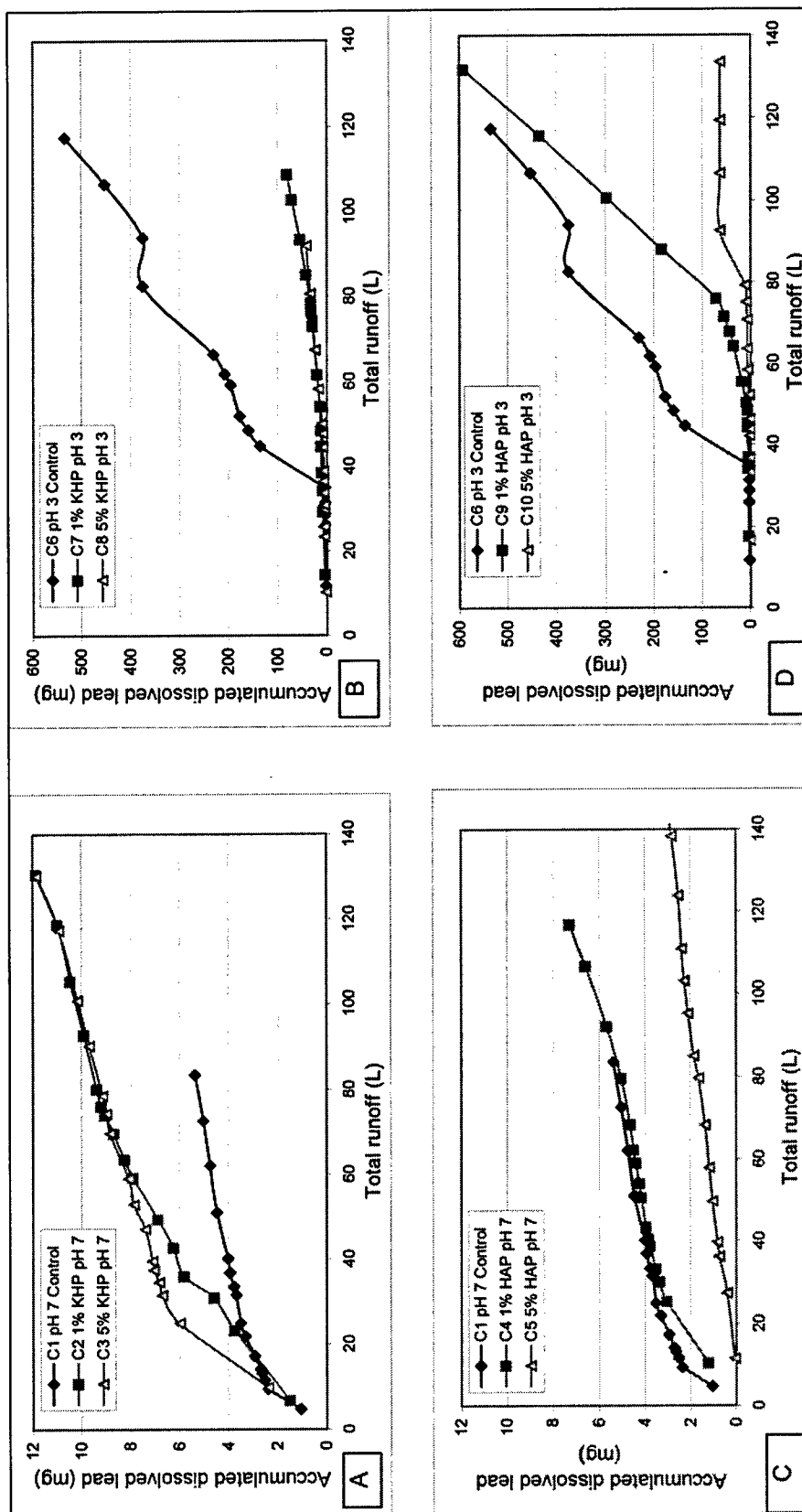


Figure 12. Accumulated dissolved lead in runoff from lysimeters: (A) KHP addition at pH 7, (B) KHP addition at pH 3, (C) HAP addition at pH 7, (D) HAP addition at pH 3

Total (digested) lead in leachates from lysimeters

The total, or digested, lead content of leachates and runoffs was determined after nitric acid digestion of the samples. The water and the suspended sediment leaving the leachate collection point were placed in a container prior to acid digestion. The container was agitated for 2 min in order to resuspend any particulate matter present in the leachate sample. A 45-ml sample was removed for acid digestion. This volume was representative of the total volume of water and suspended sediment leaving the lysimeter through the leachate exit tube (Figure 2).

Total lead concentrations in individual leachates after each rain event are listed in Appendix A (Table A7). The accumulated values of total lead released in leachates are charted in Figure 13 and summarized in Table 9. In general, total lead concentrations were much higher than the corresponding dissolved lead values, indicating a large fraction of the lead lost to the leachates was in an insoluble, particulate form.

Table 9
Average and Highest Concentrations and Mass of Digested Lead in Leachates After 16 Rain Events

Parameter	Phosphate additive				
	Control	1% KHP	5% KHP	1% HAP	5% HAP
pH 7 lysimeters					
Lysimeter	C1	C2	C3	C4	C5
Average leachate lead (mg/L) ¹	1.26	1.09	0.71	0.61	0.77
Highest single value (mg/L)	6.95	5.18	5.18	5.05	5.69
Total mass of lead leached (mg)	265	138	83.0	76.1	72.6
pH 3 lysimeters					
Lysimeter	C6	C7	C8	C9	C10
Average leachate lead (mg/L)	2.16	1.67	1.22	1.42	1.65
Highest single value (mg/L)	13.1	5.35	5.11	6.52	9.56
Total mass of lead leached (mg)	184	149	161	132	214

¹ Total digested mg lead in all leachates divided by the total volume of leachate collected

pH 7 leachates. At pH 7, total lead level in the control leachate was over 60 times higher than the very low dissolved lead levels found in corresponding leachates (an average total concentration of 1.26 mg/L lead compared with 0.019 mg/L found in the dissolved analysis). About half of the total lead was contained in the first 30 to 40 L of leachate collected. The highest total lead concentration found in the pH 7 control leachates was 6.95 mg/L after about 40 L had been collected. The total lead released continued at a lower but consistent rate throughout the remainder of the test.

HAP reduced the total lead lost in the leachates by approximately one-half. KHP lowered the total lead released to the leachates from 1.26 mg/L to 1.09 and 0.71 mg/L or about 13 and 44 percent from the control level at the 1 and 5 percent treatment levels, respectively. At pH 7, all of the average

concentrations of total lead released in leachate samples were from 40 to 400 times the levels of dissolved lead found by analysis of the same leachate samples.

Both HAP and KHP addition reduced the accumulated mass of lead released in the leachates; however, HAP had a much greater effect than KHP (Figures 13A and 13C). After an initial 50 mg of lead was released in the first 15 L of leachate in HAP-treated cells, very little total lead was lost over the remainder of the experiment.

pH 3 leachates. The average total lead concentrations varied from 2.16 mg/L in the control to 1.22 mg/L in the 5 percent KHP to 1.65 mg/L in the 5 percent HAP. At pH 3, neither additive was particularly effective in lowering the total lead losses to the leachates. In all cases, a large fraction of the total lead was released in the first 25 to 30 L of leachate, followed by a consistent loss of lead from all of the lysimeters over the remainder of the experiment.

The reduction in pH of the leachant from pH 7 to pH 3 did not have a major effect on the accumulated quantity of total lead released in runoff from the lysimeters (Figures 13B and 13D).

Total (digested) lead released in runoff from lysimeters

Relatively larger amounts of total lead were found in the runoff than in the leachates. Total lead concentrations in lysimeter runoff are detailed by rain event in Appendix A (Table A9) and are summarized in Table 10. Accumulated lead releases are illustrated in Figure 14.

Table 10					
Average and Highest Concentrations and Mass of Digested Lead in Runoff After 16 Rain Events					
Parameter	Phosphate Additive				
	Control	1% KHP	5% KHP	1% HAP	5% HAP
pH 7 lysimeters					
Lysimeter	C1	C2	C3	C4	C5
Average runoff lead conc. (mg/L) ¹	7.18	3.89	3.15	12.5	7.92
Highest single value (mg/L)	15.8	9.44	17.2	44.6	27.4
Total mass of lead in runoff (mg)	453	544	537	1815	1438
pH 3 lysimeters					
Lysimeter	C6	C7	C8	C9	C10
Average runoff lead conc. (mg/L)	11.4	8.71	5.50	15.7	21.2
Highest single value (mg/L)	26.9	23.3	20.6	43.8	57.1
Total mass of lead in runoff (mg)	1,309	996	641	1,994	2,217
¹ Total mg of digested lead in runoff in each cell divided by the total volume of runoff collected					

For the control lysimeters, the average lead level in the runoff (Table 10) was 5.7 times higher than in leachates at pH 7 (7.18 mg/L in runoff compared with 1.26 mg/L in the control leachate) and 5.3 times higher at pH 3 (11.4 mg/L compared with 2.16 mg/L). The highest total lead concentration values found in individual runoff samples (15.8 mg/L in pH 7 runoff and 26.9 mg/L in pH 3 runoff) were found in the control cell runoff samples.

The soil amended with 1 percent KHP demonstrated a reduction in the average total lead in the runoff of approximately 50 percent at pH 7 and 25 percent at pH 3. The lysimeters with 5 percent KHP were the most successful at lowering the lead levels, reducing lead levels to approximately one-half that of the control runoff at both pHs.

There was virtually no effect on accumulated total lead mass released in runoff from the lysimeters with added KHP at pH 7 (Figure 14A). However, HAP addition actually increased the mass of lead in runoff at the same pH value (Figure 14C). At pH 3 (Figure 14B) a comparison of the results from the untreated control lysimeter to the amended soils lysimeters showed that the 1 percent KHP addition had a limited effect on accumulated total mass of lead released in runoff while the 5 percent KHP treatment reduced the total mass of lead lost. The HAP treatment increased the accumulated total mass of lead released. These increases at both pH values suggest that HAP addition had a negative impact on soil cohesion that increased TSS in the runoff and resulted in higher levels of lead released.

Total lead lost to the environment

The combined total accumulated amount of lead released for the different phosphate additives from both leachate and runoff is illustrated in Figure 15. The total mass of lead lost in the effluents from all of the treatments but one was equal to or higher than that lost in the untreated control. The only treatment having consistently lower lead content was 5 percent KHP leached at pH 3. The other KHP-treated soil produced lead releases very similar to the untreated control at both pH levels. HAP treatment increased the total amount of lead released at both treatment levels and at each pH.

In all treatments, most of the lead released was in the form of insoluble, digestible lead particulates and not as dissolved lead. The relative importance of the two forms in an environmental sense is subject to discussion.

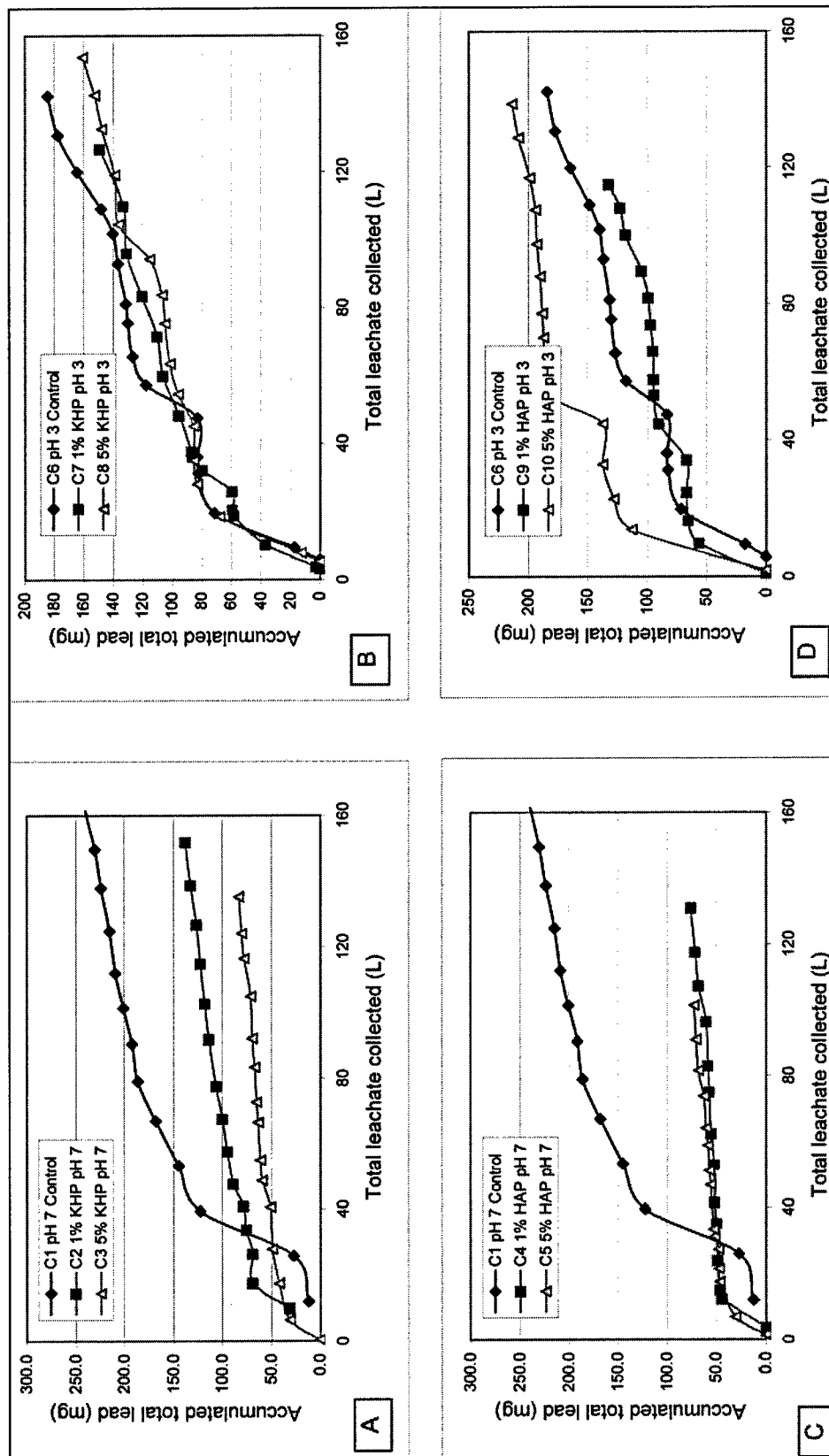


Figure 13. Accumulated total (digested) lead in leachates from lysimeters: (A) KHP addition at pH 7, (B) KHP addition at pH 3, (C) HAP addition at pH 7, (D) HAP addition at pH 3

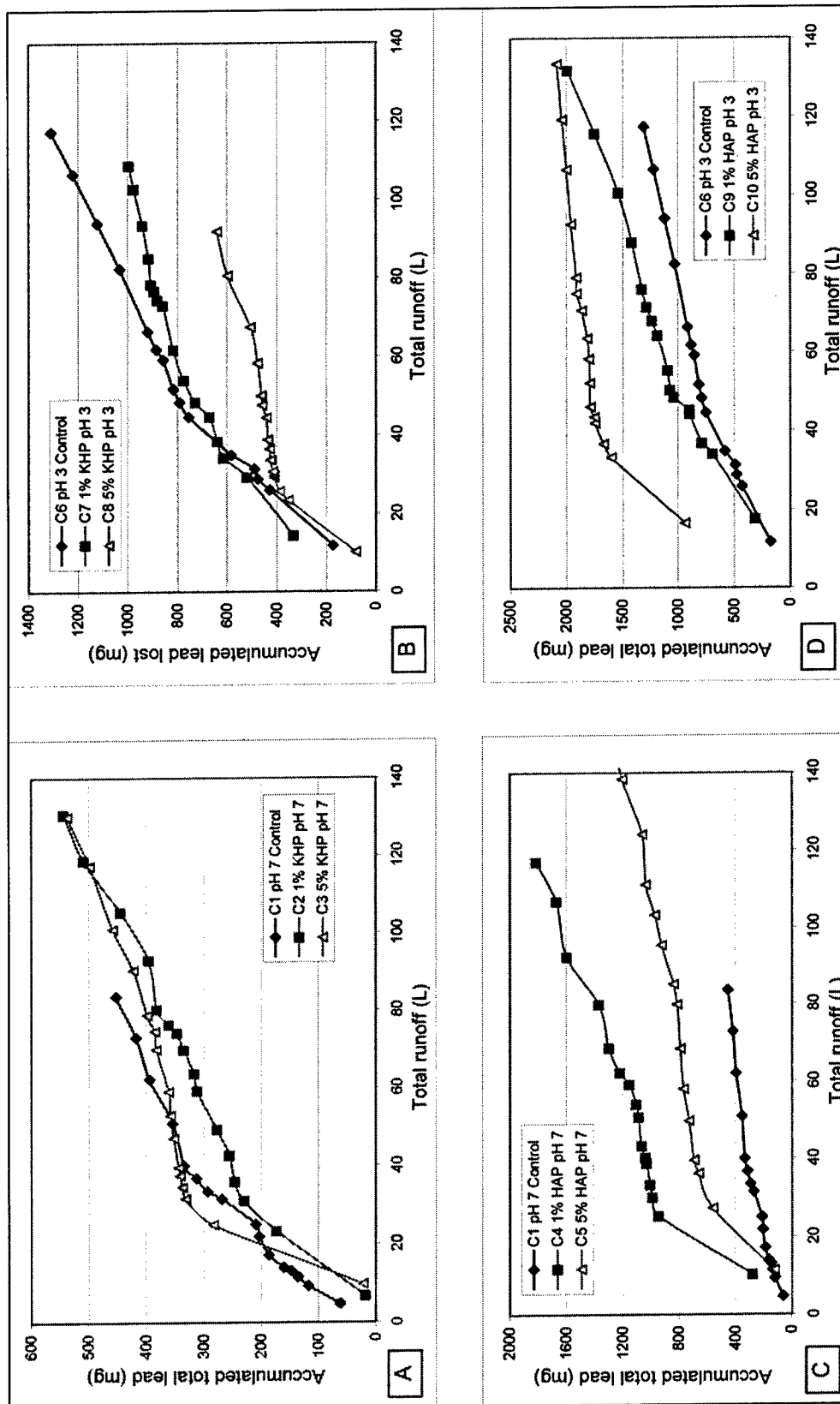


Figure 14. Accumulated total (digested) lead in runoff from lysimeters: (A) KHP addition at pH 7, (B) KHP addition at pH 3, (C) HAP addition at pH 7, (D) HAP addition at pH 3

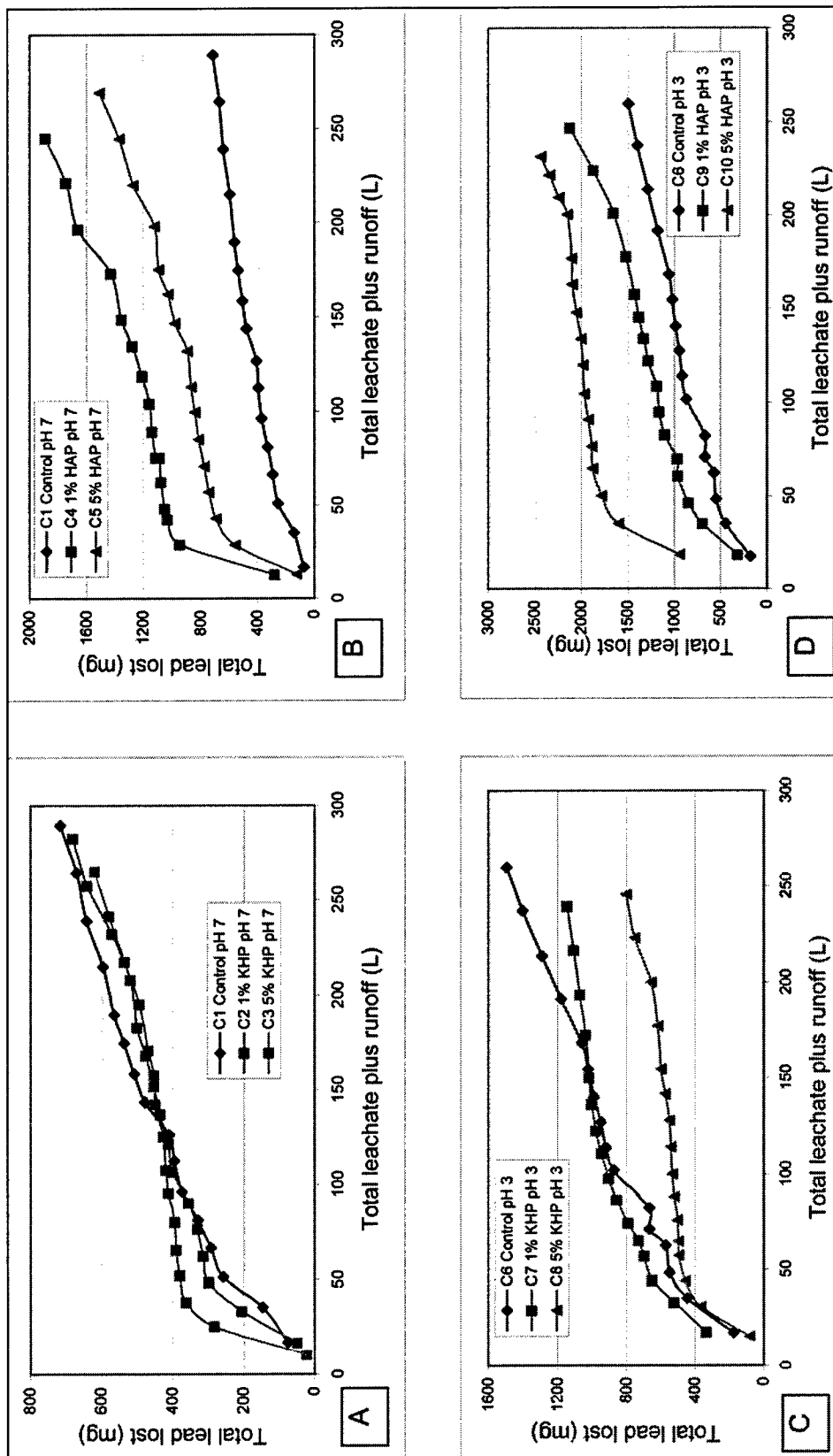


Figure 15. Total accumulated lead lost in both leachates and runoff: (A) KHP addition at pH 7, (B) KHP addition at pH 3, (C) HAP addition at pH 7, (D) HAP addition at pH 3

Correlation of Total Lead Lost with Suspended Solids Levels in Effluents

In the previous discussion, the role of suspended solids is shown to be a critical pathway for lead releases from this soil type under these conditions. For this reason, a comparison of the mass of lead leaving the lysimeter system with the mass of suspended solids leaving the system for both leachate and runoff is warranted. Lead mass was determined by multiplying the volume of the aqueous sample by the concentration of lead in the sample. The mass of suspended solids was similarly determined by multiplying the TSS concentration by the volume of the sample. The results are presented in Table 11.

Table 11					
Comparison of the Mass of Lead Leaving the System with the Total Mass of Suspended Solids Leaving the System					
Parameter	Phosphate Amendment				
	Control	1% KHP	5% KHP	1% HAP	5% HAP
pH 7 Lysimeters					
Lysimeter	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5
Leachate Pb (g)	0.26	0.14	0.09	0.08	0.08
Leachate ss ¹ (g)	29.0	26.7	3.43	1.36	2.69
Runoff Pb (g)	0.45	0.54	0.54	1.71	1.44
Runoff ss (g)	53.6	151	124	246	126
Total Pb (g)	0.71	0.68	0.62	1.79	1.51
Total ss (g)	82.6	177	127	247	128
pH 3 Lysimeters					
Lysimeter	Cell 6	Cell 7	Cell 8	Cell 9	Cell 10
Leachate Pb (g)	0.18	0.15	0.16	0.13	0.21
Leachate ss (g)	2.65	12.5	14.9	3.08	20.1
Runoff Pb (g)	1.31	1.00	1.01	1.99	2.22
Runoff ss (g)	107	93.4	88.9	174	210
Total Pb (g)	1.49	1.15	0.80	2.12	2.43
Total ss (g)	110	106	104	177	230
¹ ss = suspended solids in effluent					

The total mass of soil leaving the amended systems as suspended solids was greater than the mass released in the unamended, control system in all cases for the five cells subjected to artificial rainwater at pH 7. For the 5 cells where pH 3 rainwater was applied, the control and the two soluble phosphate treatment cells (KHP) had comparable soil losses. The two HAP systems showed significantly greater soil loss compared with the controls and potassium phosphate treatments under pH 3 rainfall.

Figure 16 displays the total lead and suspended solids leaving the 10 lysimeter systems in the runoff. If the mass transfer mechanisms were identical in all of the systems, one would expect the mass of soil leaving all the systems and the mass of lead leaving all the systems to be directly correlated. A rough correlation

between the mass of TSS and the mass of lead leaving some of the systems is noted; however, at pH 7 the 1 and 5 percent KHP cells showed less of a correlation than the other cells.

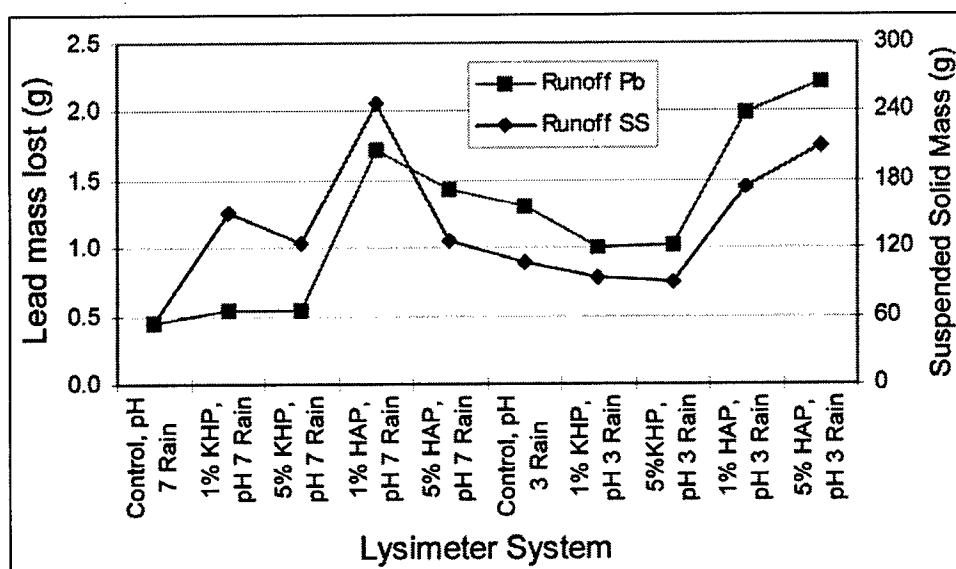


Figure 16. Suspended solids and total lead leaving the lysimeters via runoff during the 16 rain events

A plot of the mass of suspended solids in the runoff versus the mass of lead in the runoff for the 10 cells is shown in Figure 17. Seven systems appear to have a consistent ratio of lead to suspended solid mass as observed from the trend line in Figure 17. The R^2 value for a linear fit through these 7 points is 0.975; the trend line equation is ($y = 0.0111x$) with the intercept set at the origin. The three outlying systems (1 percent HAP, pH 7; 1 percent KHP pH 7; and 5 percent KHP pH 7) not included in the fit are shown below the trend line. The ratio of lead to suspended solids for the three cells (pH 7, 1 and 5 percent KHP and to a lesser extent the pH 7, 1 percent HAP,) is not consistent with the other lysimeter systems. The reduced lead to suspended solids ratio for these three systems could be explained by a number of mechanisms: preferential suspension of nonlead associated particles, lead removal from suspendable particles prior to transport, chemical scavenging of ionic lead that is competitive with cation exchange or other associative events between lead ions and suspendable soil particles, heterogeneity factors, or by other processes not currently understood.

The two pH 7 systems graphed below the trend line (1 and 5 percent KHP) that showed the greatest difference in the ratio of lead mass to suspended solids mass were the two systems that showed a reduction in lead mobility compared with the control system. These results indicate that maturation of chemical soil stabilization technology to a point where berm amendments can be used with confidence to reduce or eliminate lead migration from small arms impact areas is contingent on an understanding of the mechanism of this ability to reduce the lead mass to suspended solid mass ratio.

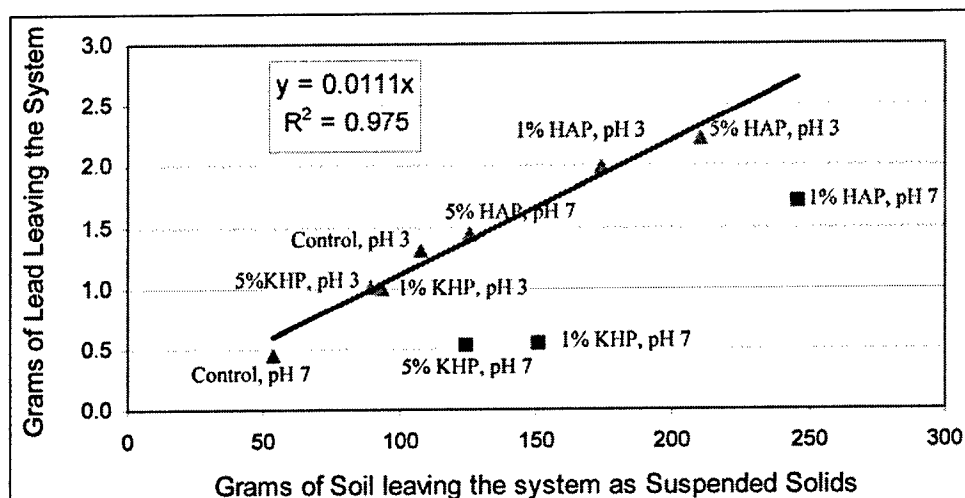


Figure 17. Correlation of total mass of lead versus the mass of total suspended solids in the runoff

Toxicity Characteristic Leaching Procedure (TCLP) Lead Losses from Treated and Untreated HAFB Soils

TCLP extractions were performed on the treated and untreated 8,000 mg/kg lead-contaminated HAFB soil before and after rain simulation tests were conducted. For comparative purposes only, TCLP extractions were carried out on an untreated and treated 80 mg/Kg lead HAFB soil that was not subjected to rain simulation tests. This evaluation of the characteristic leaching properties of the soils was done in order to assess the effects of the phosphate additives on lead losses from soils containing low and high levels of lead.

The results from the TCLP tests of the two soils before simulated rain testing are summarized in Table 12, and the individual results of the three replicate analyses and their standard deviations are listed in Appendix A (Table A3). Lead concentration results from triplicate TCLP testing on 8,000 mg/Kg lead-contaminated HAFB soil were 477, 539, and 806 mg/L with an average value of 607 mg/L, well above the 5 mg/L TCLP limit for lead. A standard deviation of 175 mg/L (29 percent) was an indication of the variability in these results and illustrates the difficulty in developing representative samples of SAFR soils. The effects of individual lead-enriched particles and/or lead-smeared soil grains as part of the soil matrix contribute to soil inconsistency. The average of triplicate testing for TCLP lead concentration from the 80 mg/L soil was 3.62 mg/L (standard deviation 0.11 mg/L), below the 5.0 mg/L TCLP action level for lead.

KHP amendment of the 80 mg/L soil had a marginal effect on TCLP lead released. However, HAP addition showed reductions of 22 and 86 percent. Phosphate amendment of the 8,000 mg/L soil samples had a dramatic effect on the lead released in the TCLP extract. A 1 percent KHP addition reduced the lead in the extract from 607 mg/L to 4.2 mg/L representing a 99.3 percent reduction in

the lead released. Five percent KHP reduced the lead levels by 99.9 percent to 0.5 mg/L. HAP addition was also effective. A 1 and 5 percent HAP reduced the lead in the TCLP extract to 64 mg/L and to about 1 mg/L, representing an 89.5 and a 99.8 percent reduction, respectively.

Table 12
Lead Concentrations in TCLP Tests of HAFB Soils

Parameter	Phosphate Additive				
	Control	1% KHP	5% KHP	1% HAP	5% HAP
80 ppm Pb (mg/L) ¹	3.62 ± 0.11	3.67 ± 0.13	3.41 ± 0.05	2.82 ± 0.15	0.50 ± 0.05
8,000 ppm Pb (mg/L)	607 ± 175	4.2 ± 2.32	0.50 ± 0.12	64 ± 25.7	0.97 ± 0.09

¹ Average of three replicates and standard deviation.

Soil samples taken from all of the lysimeters containing 8,000 mg/L HAFB soil at the end of the experiment were tested for TCLP lead. The results before and after rain simulation testing are shown in Table 13 and Figure 18; detailed data are listed in Appendix A (Table A3). TCLP lead in the control sample showed a decrease in concentration after the 16 rain events when compared with the results before the rain events. However, a comparison of the TCLP lead from phosphate amended soils before the rain events to the results after the rain events (Figure 18) showed increases instead of decreases in TCLP lead concentrations. The two amendments at both pH levels showed a decreased capability of stabilizing lead after the 16 rain events (Table 13). This factor suggests that both of these phosphate amendments may lose their ability to stabilize lead over time. In the case of the 8,000 mg/Kg HAFB soil after 16 weeks or about 1 year of simulated rainfall, lead releases from the phosphate-amended soil increased. This trend toward increased TCLP lead concentration after rain simulation testing further raises the issue of long-term stability of in situ phosphate treatment of lead-contaminated soils.

Table 13
Lead Concentrations in TCLP Testing of Soils Before and After Rain Events

Parameter	Phosphate Additive				
	8,000 mg/Kg Pb Control	1% KHP	5% KHP	1% HAP	5% HAP
TCLP Pb before rain events (mg/L)	607 ± 175	4.2 ± 2.32	0.503 ± 0.12	64 ± 25.7	0.97 ± 0.09
pH 7 lysimeters					
Lysimeter	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5
TCLP Pb after rain events (mg/L) ¹	146 ± 42	30.7 ± 15	4.20 ± 0.17	103 ± 54	11.0 ± 9.6
pH 3 lysimeters					
Lysimeter	Cell 6	Cell 7	Cell 8	Cell 9	Cell 10
TCLP Pb after rain events (mg/L)	280 ± 93	27 ± 7.4	3.11 ± 0.27	211 ± 64	3.14 ± 0.96

¹ Average of three replicates and standard deviations

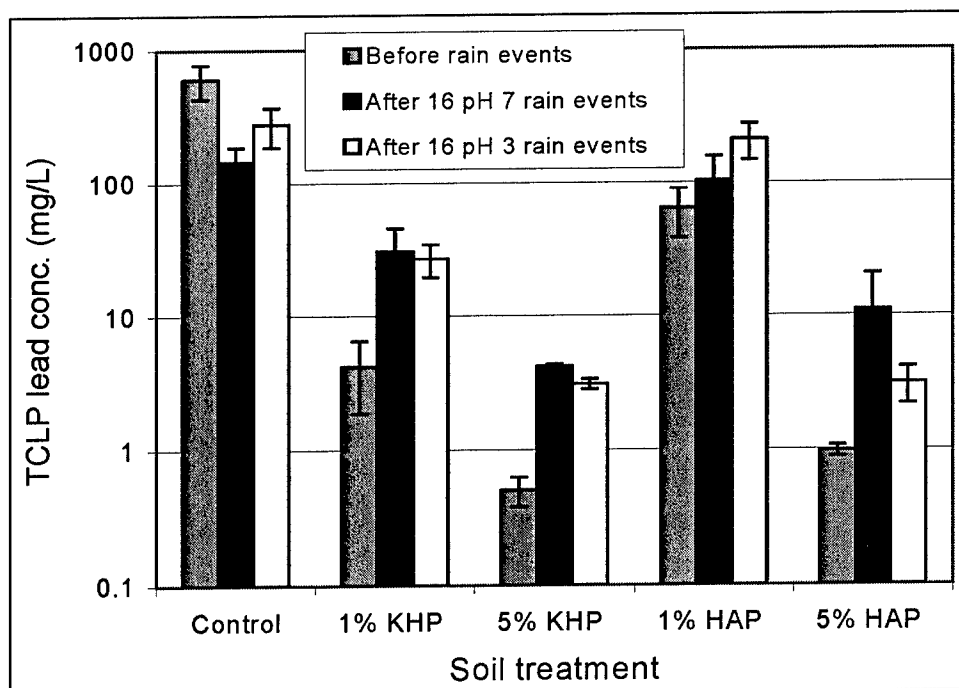


Figure 18. TCLP lead concentrations before and after rain events

Phosphate Concentrations in Effluents

Leachates. Phosphate concentrations in leachates are shown in Table A12 in Appendix A. Average phosphate concentrations for both leachate and runoff are listed in Table 14, and the accumulated phosphate in leachate is depicted in Figure 19. As expected, phosphate concentrations in the control leachates were low, averaging 0.23 mg/L in pH 7 leachates and 1.15 mg/L in pH 3 leachates (Table 14 and Figure 19).

Phosphate concentration in the leachates from the lysimeters with phosphate additives reflected the solubility of the phosphate additive. HAP is only slightly soluble in water ($K_{sp} = 1 \times 10^{-36}$ at 25° C), while KHP is highly soluble in water (220 g/L at 25° C). Large additions of HAP would be expected to render the soil slightly more basic, while KHP addition would acidify the soil and possibly cause some alteration in soil structure.

These expectations were evident in the amount of phosphate leached from the amended lysimeters. At pH 7, average phosphate concentrations leached from HAP-amended soil were 1.1 and 2.05 mg/L. However, at pH 3 the values were 2.22 and 22.5 (2 and 10 times higher) at 1 and 5 percent addition, respectively. The increase in phosphate concentration at pH 3 reflects the increase in the solubility of HAP under acidic conditions. At 1 percent KHP addition and pH 7 rainwater, the average phosphate concentration was 33.4 mg/L, 30 times more than the phosphate released from the 1 percent HAP lysimeter. The average concentrations from the cells with 5 percent KHP addition leached phosphate averaging 2,690 mg/L (2.7 g/L) at pH 7 and 6,196 mg/L (6.2 g/L) at pH 3 (Table 14). This phosphate release averaged between 19 and 61 g per rain event. Figure 19

shows the accumulated phosphate loss in leachate after KHP and HAP addition. As expected, phosphate loss for the 5 percent KHP amendment was far greater than the loss at 1 percent treatment.

Runoff. Phosphate concentrations in runoff are shown in Table 14 and in Appendix A (Table A13). Phosphate levels, 0.33 mg/L at pH 7 and 0.89 mg/L at pH 3 (Table 14), in the runoff from the control lysimeters were also quite low as expected and were comparable with those found in the leachates (Table 14). The average phosphate concentration in the runoff after KHP addition was nearly the same or much lower than the concentration in the leachate. However, average phosphate concentration in the runoff after HAP addition was always higher than the concentration in the leachate.

Figure 20 shows the accumulated mass of phosphate lost in runoff after KHP and HAP addition. In contrast to the KHP amended test cells that had much higher levels in the leachates than in the runoff, phosphate releases in the leachates and runoffs of the HAP-amended samples were similar.

Table 14					
Average Phosphate Concentration in Leachates and Runoff After 16 Rain Events					
Parameter	Phosphate Additive				
	Control	1% KHP	5% KHP	1% HAP	5% HAP
pH 7 lysimeters					
Lysimeter	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5
Avg. leachate phosphate (mg/L) ¹	0.23	33.4	2690	1.10	2.05
Avg. runoff Phosphate (mg/L)	0.33	27.2	157	1.20	3.46
pH 3 Lysimeters					
Lysimeter	Cell 6	Cell 7	Cell 8	Cell 9	Cell 10
Avg. leachate phosphate (mg/L)	1.15	173	6196	2.22	22.5
Avg. runoff phosphate (mg/L)	0.89	175	342	6.93	24.8
¹ Total mg phosphate in all leachates or runoff divided by the total volume of leachate or runoff collected					

Long-Term Loss of Phosphate in Cells With 5 Percent Amendments

To further study and quantify the loss of phosphate over an extended period of time, after a 4-week break, rain events for four lysimeters containing soils treated with 5 percent phosphate additives were continued for an additional 28 weekly rain events. Only leachate was collected during this testing. The average rate of loss of phosphate during the 16 rain simulation tests is shown in Table 15, and the phosphate concentration in each leachate for each of the extended rain events are shown in Appendix A (Table A12).

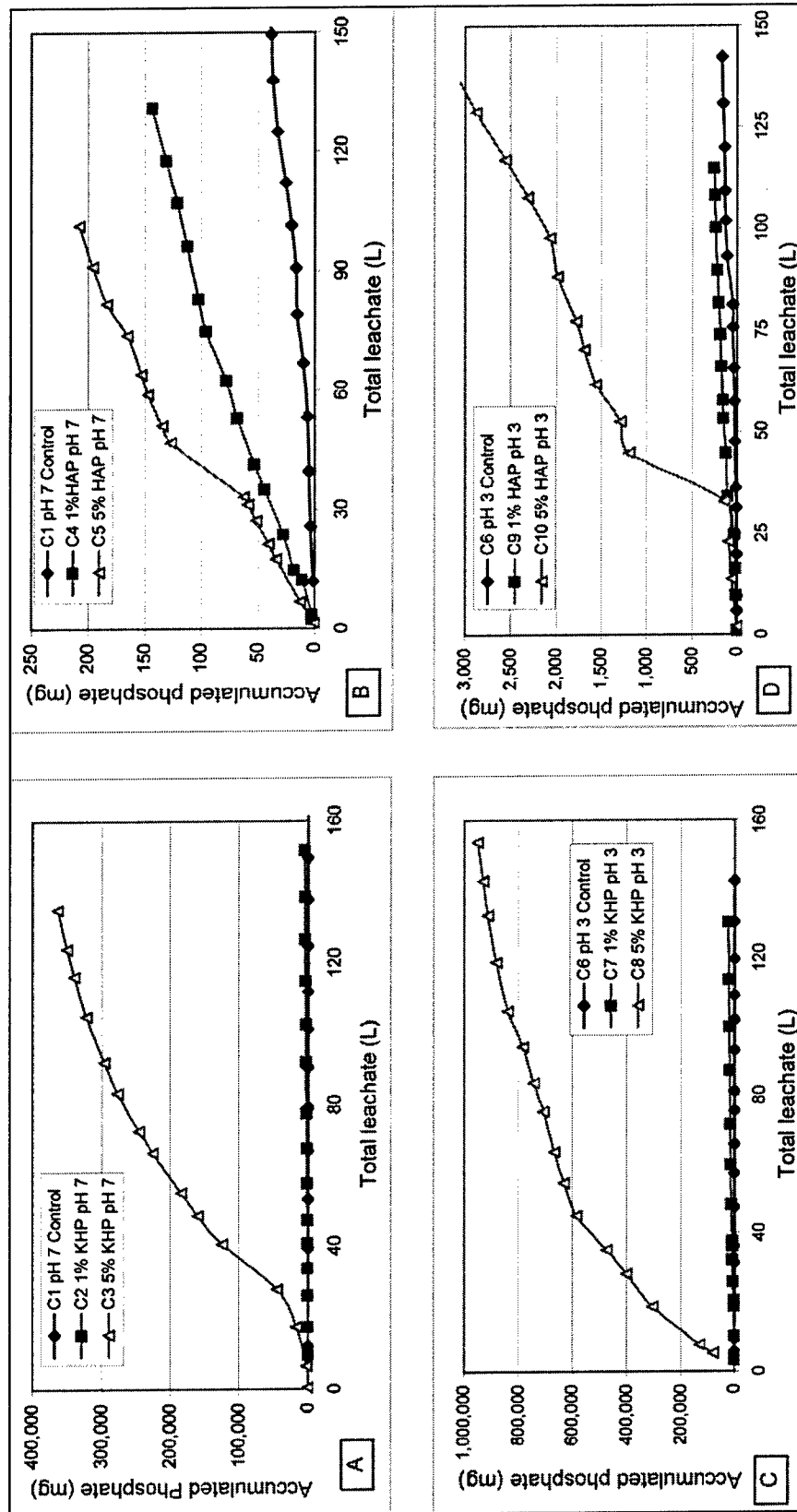


Figure 19. Accumulated phosphate in leachates: (A) KHP addition at pH 7, (B) HAP addition at pH 7, (C) KHP addition at pH 3, (D) HAP addition at pH 3

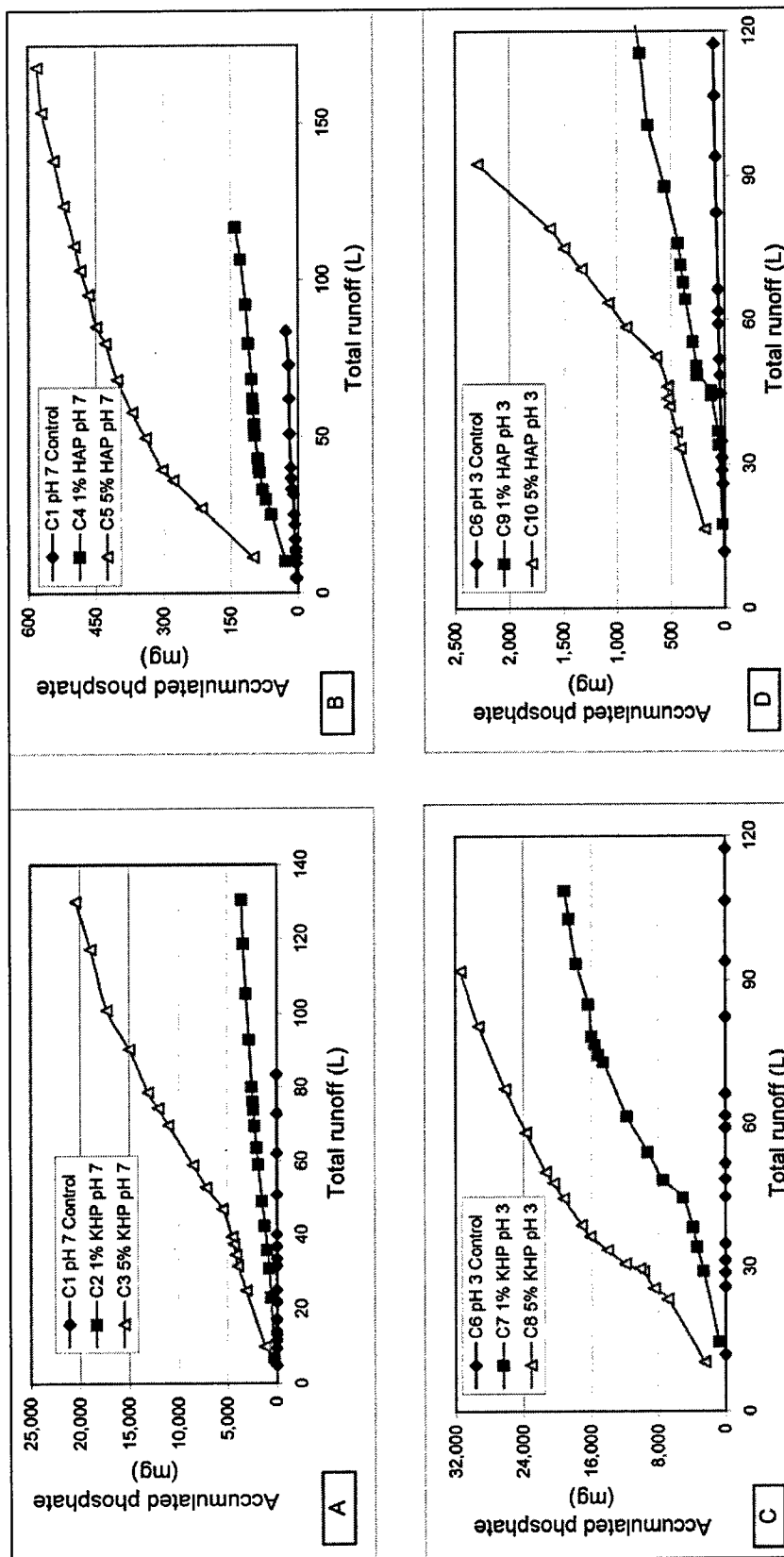


Figure 20. Accumulated phosphate in runoff: (A) KHP addition at pH 7, (B) HAP addition at pH 7, (C) KHP addition at pH 3, (D) HAP addition at pH 3

Figure 21 shows a plot of both the phosphate concentration for each rain event and the accumulated amount of phosphate by leachate volume. The rate of loss of phosphate from these test cells stabilized after about 12 to 15 rain events during which 100 to 200 L of leachate had been collected. Calculations of the rate of phosphate loss averaged after 200 L of leachate had been collected are shown in Table 15. The final rates of phosphate loss from the 5 percent HAP treated lysimeter were low, about 1 mg/L at pH 3 and almost negligible at pH 7, reflecting the very low solubility of HAP.

In contrast to the HAP phosphate results, the initial rates of phosphate leaching from the KHP-treated lysimeters were high, averaging over 1,090 mg/L in the first 100 L of leachate at pH 3 and 310 mg/L in the first 100 L at pH 7. These initial loss rates were followed by the long-term consistent loss rates of 93 mg/L at pH 3 and 78 mg/L at pH 7 for the 5 percent KHP-treated lysimeters. These higher loss rates reflect the high-water solubility of KHP.

At a loss rate of 100 mg/L, production of over 500 L of leachate would remove less than one percent of the total quantity of KHP added to the system. This amount is equivalent to nearly 5 L of leachate for each kilogram of soil. Consequently, even with these loss rates, continuous phosphate leaching alone may not impact the effectiveness of this treatment.

Table 15
Average Rate of Loss of Phosphate After Leachate Collection

Treatment	Lysimeter	Accumulated Phosphate at 200 L (mg)	Accumulated Phosphate at 500 L (mg)	Difference (mg/300L)	Final Slope (mg/L)
1% HAP pH 7	Cell 5	35.4	50.6	15.2	0.051
5% HAP pH 3	Cell 10	288	590	302	1.01
1% KHP pH 7	Cell 3	40,500	63,800	23,300	77.6
5% KHP pH 3	Cell 8	120,700	148,600	27,900	93.0

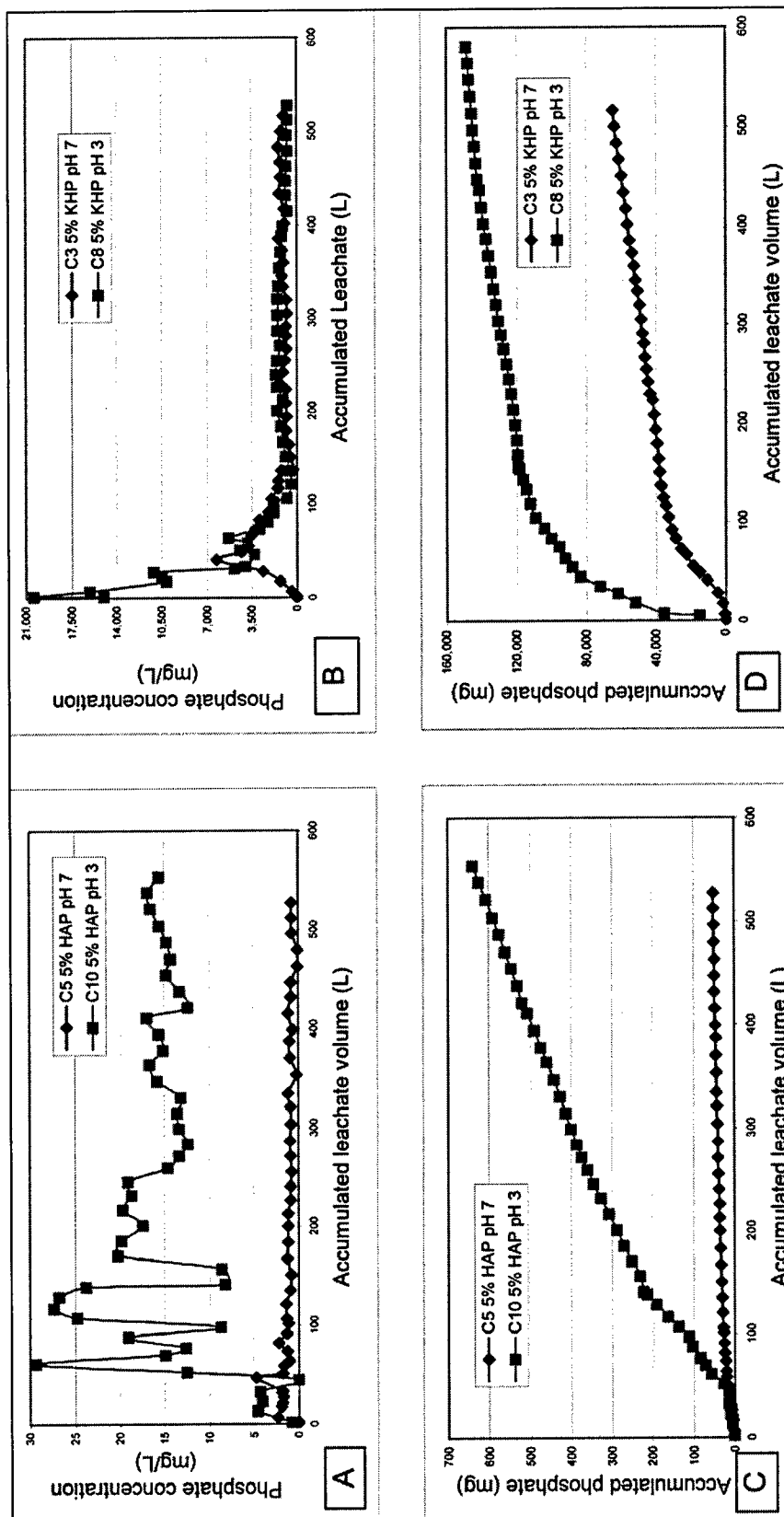


Figure 21. Long-term phosphate losses in leachates from lysimeters: (A) Phosphate concentration, 5-percent HAP, (B) Phosphate concentration, 5-percent KHP, (C) Accumulated phosphate, 5-percent HAP, (D) Accumulated phosphate, 5-percent KHP

4 Summary, Conclusions, and Recommendations

Summary

In order to effectively manage lead on SAFRs, an understanding of the physical processes such as soil erosion and the mechanisms of lead transport from SAFRs must be understood. The lead-rich berms at SAFRs that trap lead bullets from target practice training are the main sources of lead contamination at these sites. Lead (soluble or insoluble) releases or losses from these berms occur through a variety of mechanisms one of which is transport because of berm erosion via rain and storm events. Lead leaving berm impact areas through leaching and surface water runoff during rain events is a primary mechanism that results in soluble and particulate lead releases in leachate and surface water. Engineering solutions that attempt to reduce the migration of lead from SAFRs for environmental compliance purposes should address the transport mechanisms that are responsible for any unacceptable releases. A protocol using specially designed lysimeters for evaluating lead leaving firing berm soil via this transport mechanism was developed.

Two phosphate compounds were tested for their ability to stabilize lead-contaminated SAFR soil contained in the lysimeter systems. The reaction between lead ions and available phosphate to produce low solubility lead salts is a well-documented process. This mechanism for immobilization is effective for lead in solution and possibly on lead surfaces. Simulated rainfall was applied to each lysimeter over a 16-week period. Leachate and runoff samples were collected and analyzed. The results were compared with the SDWA regulatory standard of 0.015 mg/L lead.

In addition to lysimeter studies, the TCLP was used as a method for testing lead stabilization. The TCLP is a tool for determining if a particular material requires disposal in a Resource Conservation and Recovery Act of 1976 (RCRA) certified landfill. This technique has been used by a number of groups promoting berm amendment as a tool for evaluating the applicability of phosphate amendment for in situ lead stabilization. Although the technique was not developed specifically for this purpose, the procedure was used in this study to test lead leachability in the soils and compare these results to soils leached before amendment, immediately after amendment, and after 16 rain events.

Conclusions

Using neutral pH 7 synthetic, rainwater, the average concentrations of dissolved lead in leachates from the unamended and 1 percent KHP-treated soils as well as lead in runoff from all lysimeter systems exceeded the SDWA regulatory level of 0.015 mg/L but were below the TCLP lead regulatory level. Amending the soil with 5 percent KHP, 1 percent HAP, and 5 percent HAP lowered the concentration below the SDWA standard to 0.009, 0.003, and 0.008 mg/L, respectively. With the exception of the 1 and 5 percent KHP amendments at pH 7, the average lead concentrations in runoff from the lysimeter systems were above the TCLP lead regulatory level of 5 mg/L.

When acidic rainwater was used, only the 5 percent HAP amendment lowered the leachate concentration below the SDWA standard to 0.009 mg/L. In all other lysimeter systems, the average concentrations of dissolved lead and total digested lead in leachate and in runoff exceeded the SDWA standard at both pH values. Although in comparison to unamended soil, decreases in concentration were noted in some systems; the soil amendments did not reduce the lead concentrations below the SDWA regulatory concentration.

Using neutral pH synthetic rainwater, the total mass of lead leaving the model environment via leachate and runoff combined was not significantly reduced by either KHP or HAP amendment at any treatment level. A 1 percent KHP treatment reduced the mass of lead released by less than 5 percent. The greatest reduction in total mass of lead released (14 percent lower than the control) was observed for the 5 percent by weight potassium dihydrogen phosphate (KHP) amendment system. These reductions are not sufficient to expect this engineering approach to allow SAFRs with these types of soils that are out of regulatory compliance to reach compliance. In comparison to KHP, the HAP amended systems more than doubled the total amount of lead released in the pH 7 runoffs. This result may indicate that addition of this amendment tended to aggravate soil erosion.

A similar pattern was observed for the total lead leaving the system when acidic artificial rainwater was used. The total mass of lead leaving the model environment was not reduced sufficiently by any of the four treatments using pH 3 rainwater as the water source. The 1 percent KHP treatment reduced lead losses by less than 25 percent. The greatest reduction in total lead (46 percent lower than the control) was again observed for the 5 percent by weight potassium phosphate amended system. A nearly 50 percent reduction in lead release is only expected to be effective for sites that are near the compliance level. In contrast, the 1 and 5 percent HAP amendment systems showed no reduction in lead release and again increased the total lead leaving the system by 1.42 and 2.45 times the control, respectively, both representing a negative instead of a positive reduction in lead releases.

Although studies have shown that soluble lead in aqueous solutions is stabilized by formation of insoluble lead salts with phosphate ions, significant stabilization of lead that is particulate in nature and associated with suspendable soil particles would not be expected through this mechanism. On small arms firing

ranges where high-velocity rounds are fired, significant bullet fractionation occurs and lead:soil associated particles are expected. For this reason it is not surprising that the total digested lead released (lost) during the experiment greatly exceeded the amount of dissolved lead released in both leachate and runoff samples (Tables 9 and 10) for both control and amended soils. This is especially true for the lysimeters leached at pH 7 which had very low levels of dissolved lead in the leachate or runoff. Total lead levels were from 68 to 84 times the dissolved values for the pH 7 control, and from 100 to 400 times for the lysimeters with added HAP. Ratios in the pH 7 leachates and runoffs with added KHP were uniformly 40 to 60 times larger in total lead concentration than in dissolved lead.

Although the more soluble potassium salt of phosphate was the most successful at reducing the lead leaving the lysimeters, this treatment also produced the highest amounts of phosphate in the waters leaving the lysimeters. These data indicate that similar results of lead and phosphate leaving SAFR sites would be expected. Soluble phosphate concentrations in runoff water from KHP-amended soils were observed at levels above 100 ppm with concentrations reaching over 20,000 ppm in runoff waters from rainfalls occurring near the initial treatment of the soil. Since phosphorous is an essential macronutrient needed for cell growth in such organisms as algae and cyanobacteria and it typically comprises about 2 percent of the mass algae and bacteria, (Rittman and McCarty 2001), the additional release of phosphorous from leachate and runoff could become a source of eutrofication in lakes and streams. Specific sites evaluating soil amendments that use soluble forms of phosphate should evaluate potential regulatory requirements with regards to phosphate transport from SAFRs.

Before rain simulation testing, phosphate amendment of the soil reduced the initial TCLP lead results significantly in all four amendment systems compared with the unamended control soil. After the soil had gone through 16 rains cycles over 4 months, the soil was again tested using the TCLP. With pH 7 rain as the water source, the unamended control soil showed a 4-fold reduction in the TCLP leachate lead concentration; however, the treated soils all showed approximately a 2- to 10-fold increase in the TCLP leachate lead concentrations. With pH 3 rain as the water source, the unamended control soil showed a 2-fold reduction in the TCLP leachate lead concentration as compared with the treated soils, which showed an increase in the TCLP leachate lead concentrations between approximately 3- and 12-fold. The reduction of TCLP leachate lead in the control soil suggests a removal of the most available lead during the rainfall simulation series. The increase in TCLP leachate lead in the amended soil suggests a possible impermanence of the stabilization from phosphate treatment over time.

The addition of phosphate to lead-containing soils to immobilize the lead may increase the total amount of lead lost, particularly if lead is leaving the site in leachate or runoff in the form of small, mobile, lead-containing particles. Soluble phosphate reagents (such as KHP) may have a limited potential to reduce dissolved lead in leachate and runoff, but this study finds no real potential to reduce lead transport from SAFRs via TSS runoff. TSS in runoff is a major transport mechanism for lead. Moreover, the accompanying losses of large amounts of phosphate to leachate and runoff must be evaluated in order to reduce additional environmental liability in off site mobility of regulated compounds.

If the goal of amending SAFR soils is to permanently reduce the amount of total lead (dissolved and particulate) leaving the impact area, then the results of this study indicate that chemical phosphate treatment using either the soluble phosphate amendment or the less soluble calcium phosphate amendment would be ineffective.

Recommendations

Prior to employing any engineered management technique for lead migration control at SAFRs, the mechanisms of lead transport should be determined. Furthermore, a feasibility study that measures the effectiveness of any proposed engineering solution should be performed. The feasibility study should also address the efficacy of the proposed solution to reduce or eliminate lead transport via the transport mechanism(s) active at a given range. Use of large berm lysimeters is recommended as a tool to evaluate transport mechanisms, test the effectiveness of chemical treatments for lead stabilization, and quantify lead contamination in SAFR soils.

References

- Air Force Center for Environmental Excellence. (1998). "Lead contamination in soils at military small arms firing ranges," TI#17472, Air Force Center for Environmental Excellence, Brooks Air Force Base, San Antonio, TX. Available on line: www.afcee.brooks.af.mil/pro-act/fact/june98.asp
- American Public Health Association. (1998). "Standard methods for the examination of water and wastewater," Method 3010. Andrew D. Eaton, Lenore S. Clesceri, Arnold E. Greenberg, Mary Ann H. Franson, ed., 20th ed., prepared and published jointly by American Public Health Association, American Water Works Association, Water Environment Federation, Washington DC.
- American Society for Testing and Materials. (2001). ASTM D422, D854, and D2487, West Conshohocken, PA.
- Berti, W. R., and Cunningham, S. D. (1997). "In-place inactivation of Pb in Pb-contaminated soils," *Environ. Sci. Technol.* 31, 1359-1364.
- Houlihan, J., and Wiles, R. (2002). *Lead Pollution at outdoor firing ranges*. Environmental Working Group, Washington, D.C. Available at: www.ewg.org/reports/poisonouspastime/leadpoll.pdf.
- Interstate Technology and Regulatory Council. (2003). "Characterization and remediation of soils at closed small arms firing ranges," Interstate Technology and Regulatory Council, Small Arms Firing Range Team, Blacksburg, VA. 204 pp. Available on line at: www.itrcweb.org/SMART-1.pdf
- Lambert, M., Pierzynski, G., Erickson, L., and Schnoor, J. (1997). "Remediation of lead-, zinc- and cadmium-contaminated soils," *Issues in environmental science and technology; No. 7, Contaminated land and its reclamation*, R. E. Hester and R. M. Harrison, ed., The Royal Society of Chemistry, Herts, United Kingdom, 91-102.
- Lin, Z., Comet, B., Ovarfort, U., and Herbert, R. (1995). "The chemical and mineralogical behavior of Pb in shooting range soils from central Sweden," *Environmental Pollution* 89, 303-309.
- Lower, S. K., Maurice, P. A., and Traina, S. J. (1998). "Simultaneous dissolution of hydroxylapatite and precipitation of hydroxypyromorphite: Direct

- evidence of homogeneous nucleation," *Geoch. Cosmoch. Acta* 62, 1773-1780.
- Ma, Q. Y., and Rao, G. N. (1997). "Effects of phosphate rock on sequential chemical extraction of lead in contaminated soils," *J. of Environmental Quality* 26:788-794.
- Manninen, S., and Tanskanen, N. (1993). "Transfer of lead from shotgun pellets to humus and three plant species in a Finnish shooting range," *Archives of Environmental Contamination and Toxicology* 24:410-414.
- Murray, K., Babzzi, A., Carter, C., Ehlert, A., and Kopec, M. (1997). "Distribution and mobility of lead in soils at an outdoor shooting range," *Journal of Soil Contaminations* 6, 79-63.
- Pearson, M. S., Maenpaa, K., and Pierzynski, G. M. (2000). "Effects of soil amendments on the bioavailability of lead, zinc and cadmium to earthworms." *Journal of Environmental Quality* 29, 1611-17.
- Rittman, B. E., and McCarty, P. L. (2001). *Envionmental biotechnology: Principles and application*, McGraw-Hill, New York.
- Tardy, B. A., Bricka, R. M., and Larson, S. L. (2003) *Chemical stabilization of lead in small arms firing range soils*. ERDC/EL TR-03-20, U.S. Army Corps of Engineers, Engineer Research and Development Center, Vicksburg, MS.
- Traina, S. J., and Laperche, V. (1999). "Contaminant bioavailability in soils, sediments, and aquatic environments," *Proc. Natl. Acad. Sci. USA* 96, 3365-3371.
- U.S. Environmental Protection Agency. (1999). *Test methods for evaluating solid waste, physical/chemical methods*. SW-846, Washington, DC.
- _____. (2001a). "Fact sheet on common contaminants at Superfund sites." Office of Superfund Remediation and Technology Innovation. Posted on Internet at: www.epa.gov/oerrpage/superfund/accomp/ei/contam.htm
- _____. (2001b). "Indoor Environment Division: Lead fact sheet." Office of Emergency and Remedial Response. Posted on Internet at: www.epa.gov/iaq/lead.html.
- _____. (2001c). "Best management practices for lead at outdoor shooting ranges," EPA/902-B-01-001, RCRA Compliance Branch, New York.
- _____. (2001d). "Providing solutions for a better tomorrow: Reducing the risks associated with lead in soil," EPA/600-F-01/014, Office of Research and Development, Washington, DC.
- _____. (2002). *Lead in Drinking Water Regulation: Public Education Guidance*, EPA 816-R-02-010. Washington, DC. Available on line at: <http://www.epa.gov/safewater/lcrmr/implement.html>

_____. (2003). *America's Children and the Environment: Measures of Contaminants, Body Burdens, and Illnesses (2nd Ed.)*, EPA/240-R-03001, Office of Children's Health Protection, Washington, DC.

Vaccari, D. A. (1992). "Computation of aqueous metal solubilities using spreadsheet programs." Stevens Institute of Tech., Hoboken, NJ. Available on the Internet at: <http://www.attila.stevens-tech.edu>

Appendix A

Analytical Data

Untreated Soil Lead Analyses

Table A1 HAFB Composite Soil Lead Analyses					
Sample Identification	Replicate 1 (mg/kg)	Replicate 2 (mg/kg)	Replicate 3 (mg/kg)	Average (mg/kg)	Standard deviation (mg/kg)
HAFB Composite Soil: Sample 1	8,433	8,338	7,937	8,236	263
HAFB Composite Soil: Sample 2	80,809	255,112	12,946	116,289	124,921
HAFB Composite Soil: Sample 3	10,918	20,179	14,500	15,199	4,670
HAFB Composite Soil: Sample 4	12,655	11,465	10,522	11,548	1,069
HAFB Composite Soil: Sample 5	9,467	9304	55,820	24,864	26,809
HAFB Composite Soil: Sample 6	12,457	14,772	14,589	13,939	1,287
HAFB Composite Soil Average Value				31,679	
Standard deviation of the Average Values				41,824	

Table A2 HAFB Final Mix Soil Lead Analyses									
Sample source	Rep 1 (mg/kg)	Rep 2 (mg/kg)	Rep 3 (mg/kg)	Rep 4 (mg/kg)	Rep 5 (mg/kg)	Rep 6 (mg/kg)	Rep 7 (mg/kg)	Average (mg/kg)	Standard Deviation (mg/kg)
Barrels 2 & 3	7,062	7,440	6,506	7,336	6,083	6,416	10,439	7,326	1,462
Barrels 4 & 5	9,223	19,909	8,514	9,990	8,287	8,093	10,035	10,579	4,188
Barrels 6 & 7	7,101	8,615	11,936	6,019	5,837	7,749	6,954	7,744	2,081
Barrel 8	7,314	8,099	7,695	6,541	6,567	6,650	4,990	6,837	1,013
Average lead concentration								8121	
Standard deviation of the Average Values								1680	

HAFB Soil Particle-Size Distribution

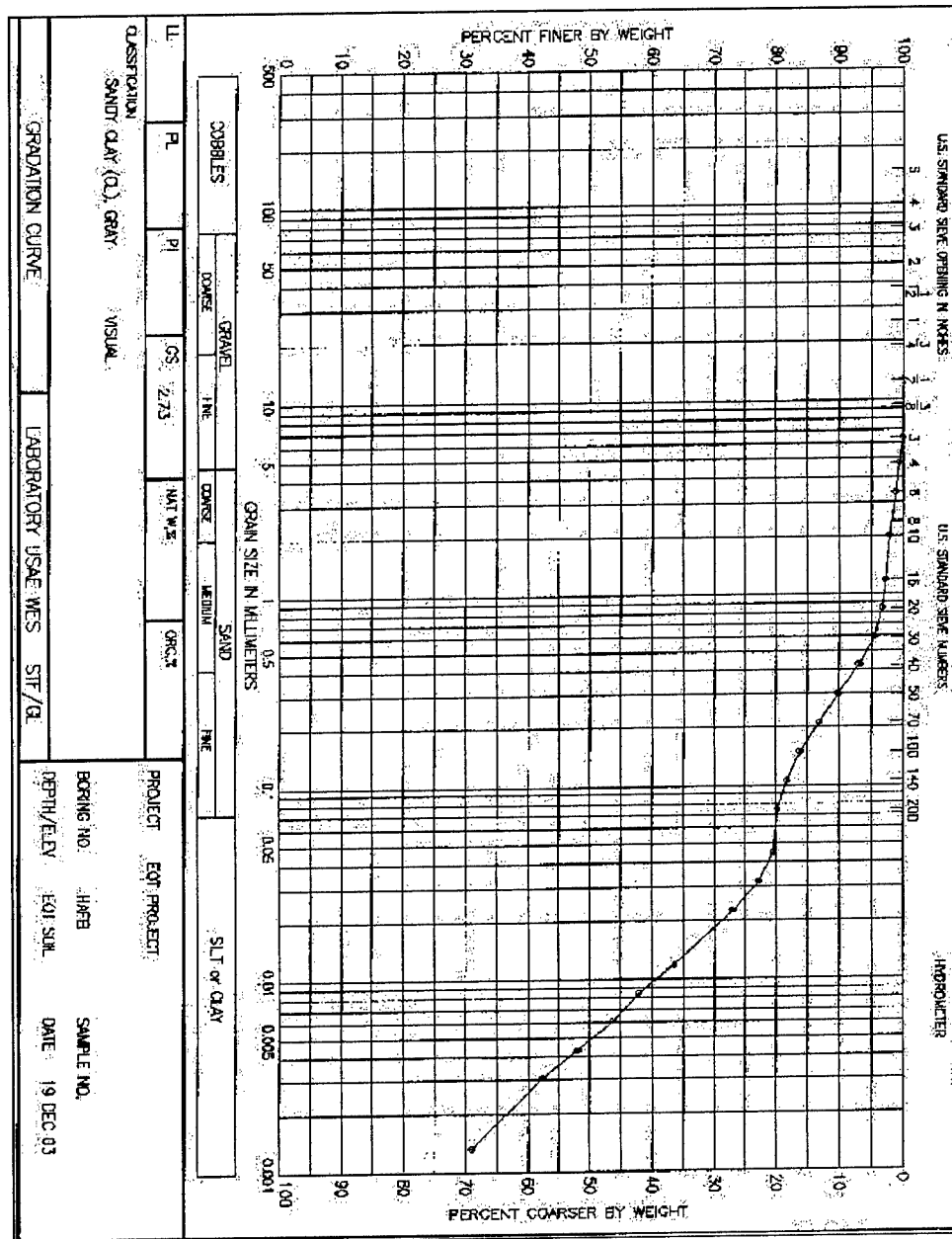


Figure A1. Grain-size distribution for HAFB SAFR soil

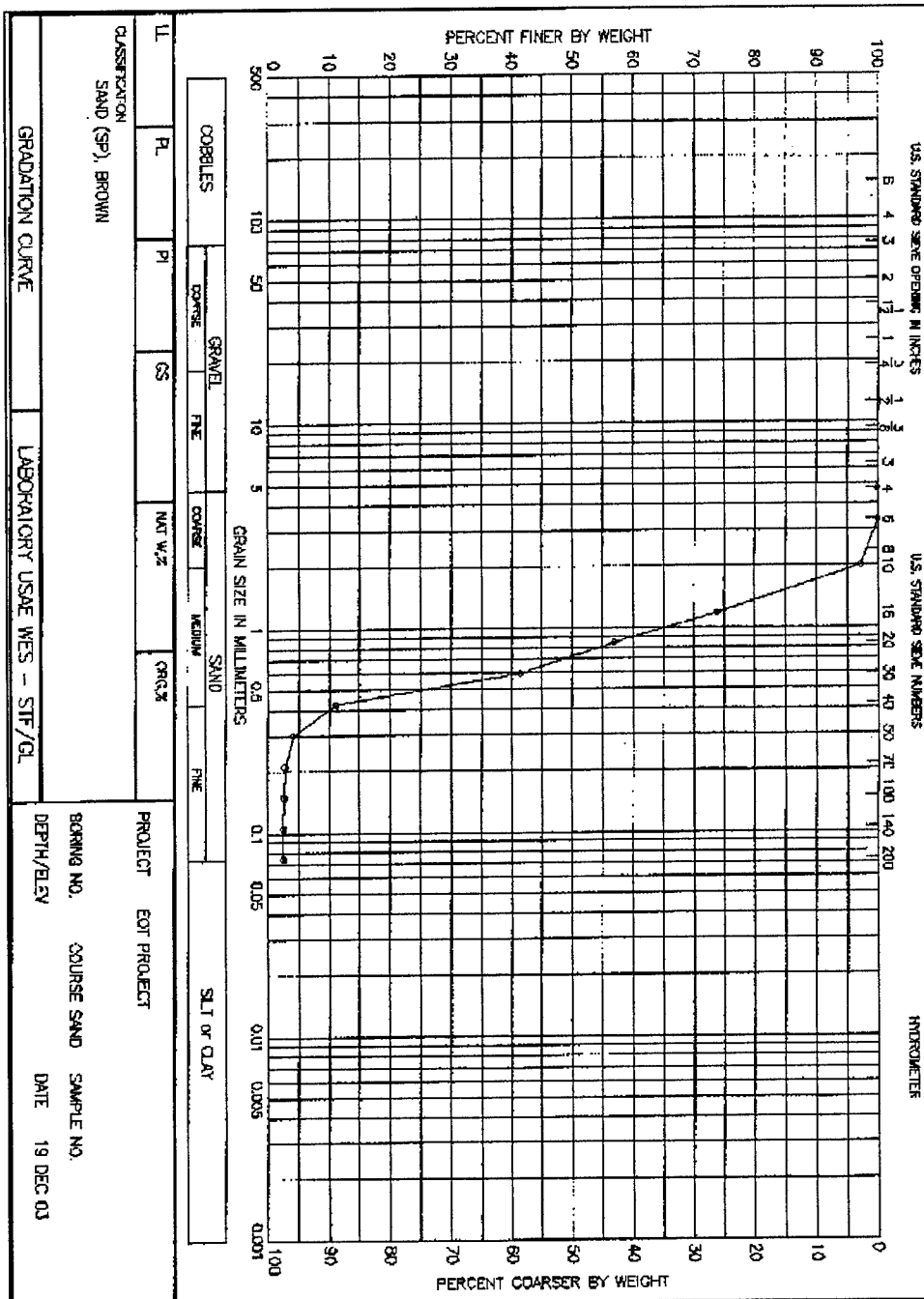


Figure A2. Grain-size distribution for coarse sand

TCLP Lead Concentration Analyses

Table A3 TCLP Filtrate Lead Analyses					
Sample Identification	Rep 1 (mg/L)	Rep 2 (mg/L)	Rep 3 (mg/L)	Average (mg/L)	Standard Deviation (mg/L)
Soil tested before rain simulation					
HAFB Soil 8000 ppm lead + no additive	477	539	806	607	175
HAFB 8000 ppm lead + 1 percent KHP	6.86	2.88	2.81	4.2	2.32
HAFB 8000 ppm lead + 5 percent KHP	0.615	0.369	0.525	0.503	0.124
HAFB 8000 ppm lead + 1 percent HAP	34.5	76.1	81.2	64.0	25.7
HAFB 8000 ppm lead + 5 percent HAP	0.868	1.03	1.03	0.973	0.091
HAFB Soil 80 ppm lead + no additive	3.56	3.55	3.75	3.62	0.11
HAFB 80 ppm lead + 1 percent KHP	3.79	3.54	3.66	3.67	0.13
HAFB 80 ppm lead + 5 percent KHP	3.37	3.47	3.40	3.41	0.05
HAFB 80 ppm lead + 1 percent HAP	2.98	2.80	2.69	2.82	0.15
HAFB 80 ppm lead + 5 percent HAP	0.458	0.491	0.558	0.50	0.051
Soil tested from cells after 16 rain events					
HAFB Control 8000 ppm: Cell #1 pH 7	152	101	184	146	42.0
HAFB 8000 ppm 1 percent KHP: Cell #2 pH 7	32.2	14.9	44.9	30.7	15.0
HAFB 8000 ppm 5 percent KHP: Cell # 3 pH 7	4.08	4.39	4.10	4.19	0.17
HAFB 8000 ppm 1 percent HAP: Cell # 4 pH 7	165	68.5	74.5	103	54.0
HAFB 8000 ppm 5 percent HAP: Cell # 5 pH 7	5.56	22.1	5.38	11.0	9.60
HAFB Control 8000 ppm: Cell #6 pH 3	221	387	231	280	93
HAFB 8000 ppm 1 percent KHP: Cell #7 pH 3	19.2	33.8	28.0	27.0	7.4
HAFB 8000 ppm 5 percent KHP: Cell #8 pH 3	3.41	3.02	2.89	3.11	0.270
HAFB 8000 ppm 1 percent HAP: Cell #9 pH 3	155	281	198	211	64.0
HAFB 8000 ppm 5 percent HAP: Cell #10 pH 3	2.14	3.23	4.05	3.14	0.96

Effluents Collected After Each Rain Event

Table A4										
Volume of Leachate Collected After Each Rain Event										
Rainfall event	pH 7 Lysimeters					pH 3.0 Lysimeters				
	C1 Control	C2 1% KHP	C3 5% KHP	C4 1% HAP	C5 5% HAP	C6 Control	C7 1% KHP	C8 5%KHP	C9 1% HAP	C10 5% HAP
Leachate 1	11.95	9.85	0.45	2.45	1.50	5.75	3.35	5.3	1.0	1.85
Leachate 2	13.90	0.30	0.01	1.18	0	3.6	0.54	2.45	0.05	0.04
Leachate 3	13.70	7.30	5.95	8.70	5.35	10.35	6.4	10.9	8.55	11.75
Leachate 4	13.75	8.95	11.05	2.60	10.6	11.6	8.55	9.45	6.8	9.2
Leachate 5	13.60	7.50	10.45	8.85	3.80	4.85	1.65	6.95	8.25	10.05
Leachate 6	12.20	7.10	12.70	11.35	6.0	11.3	5.5	10.0	9.55	11.85
Leachate 7	11.50	6.60	8.05	0	4.0	9.85	6.25	9.5	10.5	7.75
Leachate 8	10.80	10.15	6.45	6.30	2.05	8.35	3.95	9.0	8.55	9.05
Leachate 9	10.70	9.75	11.35	11.60	13.50	9.95	1.55	11.95	4.5	8.7
Leachate 10	12.85	10.20	6.25	9.50	4.25	5.55	10.45	8.2	8.4	6.95
Leachate 11	12.90	14.25	10.70	12.45	7.85	11.9	11.7	10.55	7.8	10.9
Leachate 12	11.70	10.70	8.75	8.05	5.15	8.9	11.8	10.45	7.75	9.65
Leachate 13	14.60	12.40	12.80	13.3	9.8	7.2	15.7	14.25	7.95	9.95
Leachate 14	12.95	11.80	11.50	10.95	7.9	10.65	12.7	13.65	10.6	9.15
Leachate 15	14.60	11.95	7.75	10.45	9.3	10.85	13.8	9.9	8.0	11.85
Leachate 16	14.25	13.00	10.95	13.3	10.35	11.65	16.7	11.15	6.6	9.95
Totals	205.9	151.8	135.2	131.0	101.4	142.3	130.6	153.6	114.8	138.6

Table A5										
Volume of Runoff Collected After Each Rainfall Event (L)										
Rainfall event	pH 7 Lysimeters					pH 3 Lysimeters				
	C1 0%	C2 1% KHP	C3 5% KHP	C4 1% HAP	C5 5% HAP	C6 0%	C7 1% KHP	C8 5%KHP	C9 1% HAP	C10 5% HAP
Runoff 1	4.75	6.75	9.75	10.35	11.4	11.7	14.35	10.15	17.5	16.45
Runoff 2	4.65	16.5	15.2	14.95	15.9	14.2	14.85	13.15	16.6	16.8
Runoff 3	2.15	7.7	6.65	4.8	8.85	2.85	5.0	2.25	2.8	3.4
Runoff 4	1.6	4.95	2.9	3.1	3.45	2.55	4.15	3.55	7.4	5.4
Runoff 5	0.85	6.65	2.95	5.5	10.1	3.5	6.25	0.55	1.05	1.55
Runoff 6	3.2	6.7	2.05	1.6	8.2	0	3.7	1.0	3.15	2.55
Runoff 7	4.7	9.9	7.5	2.95	10.4	9.85	5.7	2.9	1.8	6.05
Runoff 8	3.1	4.45	5.85	7.35	11.45	3.7	7.6	2.8	5.1	6.1
Runoff 9	6.5	6.0	6.1	3.35	5.3	3.4	11.35	2.4	8.8	5.15
Runoff 10	1.95	4.4	10.8	5.1	10.3	7.4	1.45	5.6	3.65	7.1
Runoff 11	3.3	2.15	4.65	3.1	7.8	2.55	2.3	3.2	3.6	4.35
Runoff 12	3.35	4.0	4.3	6.25	7.85	4.6	1.7	2.4	4.5	4.15
Runoff 13	10.8	12.7	11.6	11.3	13.0	16.1	6.7	8.2	12.0	13.5
Runoff 14	11.1	12.55	10.6	12.45	14.3	11.6	8.4	9.2	12.6	13.9
Runoff 15	10.6	13.3	16.4	14.5	15.3	12.6	9.35	13.2	15.1	12.8
Runoff 16	10.7	11.9	12.7	10.2	14.4	10.8	5.9	11.3	16.1	14.1
Totals	83.4	131	130	117	168	117	109	91.9	132	133

Lead Concentrations in Effluents

Table A6
Dissolved Lead Leachate Concentrations After Each Rain Event (mg/L)

Rain event	pH 7 Cells					pH 3 Cells				
	Cell 1 Control	Cell 2 1% KHP	Cell 3 5% KHP	Cell 4 1% HAP	Cell 5 5% HAP	Cell 6 Control	Cell 7 1% KHP	Cell 8 5% KHP	Cell 9 1% HAP	Cell 10 5% HAP
Leachate 1	0.013	0.020	0.002	0.001	0.002	0.002	0.001	0.007	0.005	0.013
Leachate 2	0.015	0.025	nd ¹	0.001	nd	0.002	0.002	0.015	nd	nd
Leachate 3	0.042	0.021	0.005	0.008	0.010	0.004	0.020	0.030	0.032	0.018
Leachate 4	0.024	0.020	0.005	0.001	0.002	0.007	0.053	0.046	0.014	0.008
Leachate 5	0.011	0.015	0.009	0.001	0.007	0.004	0.055	0.026	0.011	0.007
Leachate 6	0.010	0.010	0.014	0.006	0.004	nd	3.620	0.016	5.920	3.910
Leachate 7	0.045	0.021	0.023	0.001	0.001	2.223	0.126	0.019	1.049	0.001
Leachate 8	0.011	0.020	0.013	0.001	0.001	0.016	0.165	0.022	0.001	0.001
Leachate 9	0.014	0.023	0.007	0.001	0.004	0.035	0.162	0.038	0.001	0.001
Leachate 10	0.002	0.020	0.010	0.001	0.002	0.001	0.050	0.041	0.025	0.004
Leachate 11	0.013	0.023	0.008	0.001	0.002	0.001	0.122	0.049	0.002	0.002
Leachate 12	0.010	0.013	0.001	0.001	0.001	0.001	0.175	0.009	0.001	0.001
Leachate 13	0.012	0.016	0.002	0.001	0.001	1.120	0.418	0.019	0.147	0.001
Leachate 14	0.027	0.023	0.009	0.004	0.007	0.906	0.168	0.025	0.089	0.001
Leachate 15	0.026	0.025	0.014	0.005	0.004	0.892	0.086	0.072	0.001	0.001
Leachate 16	0.024	0.028	0.012	0.009	0.044	2.090	0.390	0.046	0.712	0.077

¹ nd = not determined

Table A7
Total (Digested) Lead Leachate Concentrations After Each Rain Event (mg/L)

Rain event	pH 7 Cells					pH 3 Cells				
	Cell 1 Control	Cell 2 1% KHP	Cell 3 5% KHP	Cell 4 1% HAP	Cell 5 5% HAP	Cell 6 Control	Cell 7 1% KHP	Cell 8 5% KHP	Cell 9 1% HAP	Cell 10 5% HAP
Leachate 1	1.006	3.130	0.135	0.011	0.044	0.042	0.016	0.022	0.373	0.326
Leachate 2	1.092	0.850	nd ¹	0.020	nd	4.756	4.719	5.106	nd	nd
Leachate 3	6.953	5.178	5.185	5.052	5.688	5.225	5.354	5.069	6.524	9.560
Leachate 4	1.638	nd	0.998	0.795	1.477	0.946	2.516	1.616	1.372	1.618
Leachate 5	1.705	0.875	0.676	0.258	0.235	0.125	0.687	0.334	0.143	0.929
Leachate 6	1.485	0.420	0.127	0.111	0.091	13.07	3.469	0.318	5.525	3.359
Leachate 7	0.488	1.574	1.047	1.001	0.947	3.523	3.258	1.120	2.246	5.577
Leachate 8	0.850	0.623	0.343	0.316	0.565	1.079	1.640	0.624	0.481	0.786
Leachate 9	0.775	0.520	0.222	0.043	0.216	0.344	0.427	0.263	0.023	0.017
Leachate 10	0.448	0.588	0.222	0.329	0.344	0.220	0.821	0.255	0.056	0.167
Leachate 11	0.680	0.543	0.171	0.150	0.200	0.453	0.902	0.753	0.277	0.150
Leachate 12	0.577	0.394	0.275	0.141	0.361	0.387	0.328	2.045	0.225	0.285
Leachate 13	0.769	0.375	0.128	0.160	0.222	1.158	0.649	0.172	0.752	0.107
Leachate 14	0.473	0.305	0.577	0.696	0.708	1.521	0.821	0.664	1.263	0.562
Leachate 15	0.379	0.512	0.343	0.328	0.263	1.190	0.163	0.498	0.524	0.767
Leachate 16	0.306	0.472	0.544	0.494	0.565	1.195	0.452	0.334	0.702	0.585

¹ nd = not determined

Table A8
Dissolved Lead Runoff Concentrations After Each Rain Event (mg/L)

Rain event	pH 7 Cells					pH 3 Cells				
	Cell 1 Control	Cell 2 1% KHP	Cell 3 5% KHP	Cell 4 1% HAP	Cell 5 5% HAP	Cell 6 Control	Cell 7 1% KHP	Cell 8 5% KHP	Cell 9 1% HAP	Cell 10 5% HAP
Runoff 1	0.223	0.222	0.245	0.119	0.006	0.133	0.301	0.202	0.228	0.024
Runoff 2	0.284	0.137	0.238	0.121	0.021	0.067	0.259	0.188	0.066	0.013
Runoff 3	0.068	0.108	0.106	0.067	0.039	0.052	0.187	0.055	0.143	0.019
Runoff 4	0.070	0.247	0.042	0.054	0.022	0.043	0.309	0.056	0.056	0.010
Runoff 5	0.089	0.068	0.071	0.047	0.021	0.053	0.203	0.070	0.064	0.020
Runoff 6	0.071	0.093	0.031	0.037	0.018	nd ¹	10.50	5.33	50.7	14.8
Runoff 7	0.079	0.102	0.040	0.036	0.019	13.54	0.302	0.478	1.829	0.442
Runoff 8	0.066	0.078	0.078	0.030	0.023	6.508	0.786	0.124	1.718	0.381
Runoff 9	0.026	0.073	0.036	0.022	0.042	5.026	0.794	0.291	1.890	0.298
Runoff 10	0.057	0.081	0.069	0.029	0.024	2.604	0.324	0.187	2.300	0.010
Runoff 11	0.043	0.072	0.034	0.035	0.023	4.377	0.988	0.264	3.425	0.398
Runoff 12	0.027	0.046	0.038	0.021	0.012	5.050	0.790	0.250	3.420	0.535
Runoff 13	0.041	0.042	0.045	0.035	0.012	8.940	1.560	0.888	9.420	3.800
Runoff 14	0.025	0.043	0.047	0.052	0.021	6.463	1.383	0.677	8.912	2.886
Runoff 15	0.027	0.040	0.047	0.063	0.022	6.201	1.744	0.756	9.168	3.197
Runoff 16	0.031	0.073	0.073	0.065	0.028	7.570	1.724	1.040	9.766	3.387

¹ nd = not determined

Table A9
Total (Digested) Lead Runoff Concentrations After Each Rain Event (mg/L)

Rain event	pH 7 Cells					pH 3 Cells				
	Cell 1 Control	Cell 2 1% KHP	Cell 3 5% KHP	Cell 4 1% HAP	Cell 5 5% HAP	Cell 6 Control	Cell 7 1% KHP	Cell 8 5% KHP	Cell 9 1% HAP	Cell 10 5% HAP
Runoff 1	13.22	2.68	2.29	27.06	10.90	14.97	23.27	8.17	17.89	57.14
Runoff 2	12.10	9.44	17.17	44.63	27.36	17.89	12.49	20.64	22.99	39.36
Runoff 3	7.67	7.36	7.24	8.84	11.67	16.81	19.07	15.59	33.92	20.65
Runoff 4	7.31	3.16	2.02	5.31	9.45	5.21	6.14	5.99	14.86	14.61
Runoff 5	15.79	1.42	1.43	4.66	3.42	26.94	5.07	1.36	2.60	2.05
Runoff 6	8.32	3.24	1.04	4.79	4.65	nd ¹	15.71	5.50	43.83	14.11
Runoff 7	3.45	3.52	1.19	9.30	2.25	17.36	7.94	3.45	18.43	0.55
Runoff 8	1.92	1.03	0.98	2.99	2.08	9.60	5.54	1.30	4.09	1.24
Runoff 9	8.99	3.06	0.51	5.08	4.69	7.94	3.70	2.63	10.61	3.29
Runoff 10	12.68	2.62	1.97	9.65	8.16	5.42	15.69	1.13	13.38	6.98
Runoff 11	6.14	6.66	0.48	21.52	6.30	10.84	5.30	5.32	14.35	10.09
Runoff 12	6.28	5.28	3.13	12.48	8.06	7.41	8.06	1.34	8.95	1.46
Runoff 13	1.89	1.10	2.09	6.26	2.03	7.01	1.29	1.81	7.28	3.20
Runoff 14	3.61	3.84	3.33	18.16	10.05	7.80	2.96	3.22	9.77	5.97
Runoff 15	2.11	4.88	2.49	5.28	6.17	7.92	3.61	6.92	14.08	7.47
Runoff 16	3.34	2.94	3.03	3.98	9.56	8.03	3.58	3.66	15.04	5.57

¹ nd = not determined

Total Suspended-Solids Analyses

Table A10
Total Suspended Solids In Leachates After Each Rain Event (mg/L)

Rain event	pH 7 Cells					pH 3 Cells				
	Cell 1 Control	Cell 2 1% KHP	Cell 3 5% KHP	Cell 4 1% HAP	Cell 5 5% HAP	Cell 6 Control	Cell 7 1% KHP	Cell 8 5% KHP	Cell 9 1% HAP	Cell 10 5% HAP
Leachate 1	327	1214	nd ¹	72	18	21	45	28	96	4838
Leachate 2	114	270	nd	39	nd	21	72	858	nd	nd
Leachate 3	320	146	30	12	75	93	65	460	195	339
Leachate 4	317	126	90	3	115	60	243	444	61	113
Leachate 5	166	493	29	23	14	14	136	13	16	15
Leachate 6	190	33	10	<1.00	<1.00	<1.00	47.2	8.4	<1.00	<1.00
Leachate 7	2.4	229.2	28.8	<1.00	3.2	33.2	268	32.4	63.2	19.2
Leachate 8	98.4	158	24.4	11.6	19.2	1.2	164.8	24.8	4	51.6
Leachate 9	84.8	113.2	5.6	<1.00	26.4	<1.00	168	71.6	2	17.2
Leachate 10	29.2	113.6	23.2	18.8	12.4	<1.00	71.2	22	<1.00	688.8
Leachate 11	97.2	62	17.6	5.2	1.2	3.6	102	65.6	4.8	5.6
Leachate 12	139.2	48	28	<1.00	12.8	<1.00	233.6	<1.00	<1.00	32.4
Leachate 13	91.6	22.4	3.2	1.6	16	<1.00	72.8	<1.00	<1.00	<1.00
Leachate 14	112	20.4	26.4	5.6	5.2	2.4	16.4	0.4	2.8	<1.00
Leachate 15	74	35.6	24.4	18.8	18.4	<1.00	<1.00	53.6	<1.00	<1.00
Leachate 16	75.6	60.4	24.4	16.8	8.4	28	42.4	40.4	<1.00	<1.00

¹ nd = not determined

Table A11
Total Suspended Solids In Runoff After Each Rain Event (mg/L)

Rain event	pH 7 Cells					pH 3 Cells				
	Cell 1 Control	Cell 2 1% KHP	Cell 3 5% KHP	Cell 4 1% HAP	Cell 5 5% HAP	Cell 6 Control	Cell 7 1% KHP	Cell 8 5% KHP	Cell 9 1% HAP	Cell 10 5% HAP
Runoff 1	1,177	4,884	1,556	4,948	1,035	1,776	3,376	836	3,510	5,924
Runoff 2	336	2,256	2,776	3,500	1,876	247	72	48	546	3,540
Runoff 3	1,057	74	1,632	1,523	294	1,429	1,403	822	3,636	1,513
Runoff 4	1,231	494	201	442	1,103	782	668	993	1,505	1,668
Runoff 5	1,127	42	305	115	319	4,072	54	18	51	12
Runoff 6	1,252	678	233	4	<1.00	nd ¹	1,300	261.2	502.4	<1.00
Runoff 7	162.4	1,101	544.8	2,455	221.6	1,569	761.6	347.2	1,960	452.4
Runoff 8	523.2	338.8	165.2	339.2	328	985.2	644.8	230.8	1,176	619.2
Runoff 9	1,286	1,078	289.6	474.8	450.4	495.2	285.6	274	989.2	288
Runoff 10	1,371	1,019	957.2	1,432	1,000	670.8	2,376	326.4	1,429	0.4
Runoff 11	1,023	2,025	602.8	2,773	684.8	1,397	625.6	680.4	1,475	915.6
Runoff 12	915.2	1,417	904	1,554	888.4	832.4	1,007	634	873.2	752.4
Runoff 13	134	110.8	62.8	2,446	79.2	818.4	249.2	713.6	886.4	631.2
Runoff 14	450.8	938.8	740	2,154	1,114	404	260	368	768.8	380
Runoff 15	593.2	1,061	696.4	1,441	700	532.4	408.8	954.4	916.4	514.4
Runoff 16	431.2	997.6	787.6	2,042	1,090	467.6	367.2	393.6	854	255.2

¹ nd = not determined

Effluent Phosphate Concentrations

Table A12
Phosphate leachate concentrations after each rain event (mg/L)

Rainfall Event	pH 7 lysimeters					pH 3.5 lysimeters				
	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	Cell 6	Cell 7	Cell 8	Cell 9	Cell 10
Leachate 1	nd ¹	13.60	89.476	0.891	0.23	0.197	13.8	15,020	0.243	0.43
Leachate 2	0.170	3.93	nd	0.336	nd	0.185	28.1	20,431	3.833	0.77
Leachate 3	nd	14.19	432	0.991	2.38	0.390	83.0	16,133	1.312	4.60
Leachate 4	nd	21.21	1,336	2.717	1.97	0.224	137.5	10,135	1.041	4.08
Leachate 5	0.279	23.15	2,652	1.122	1.83	0.342	221.4	10,515	0.903	4.32
Leachate 6	0.433	26.54	6,266	1.422	1.72	0.928	491.1	11,118	7.962	89.11
Leachate 7	nd	34.92	4,326	1.388	1.89	0.753	338.7	4,866	1.601	12.54
Leachate 8	0.370	38.82	3,799	1.438	1.77	0.455	278.5	4,021	3.251	29.40
Leachate 9	0.497	45.72	3,610	1.300	4.75	1.365	302.0	3,337	1.841	14.93
Leachate 10	0.545	45.25	3,283	1.024	1.80	0.465	226.0	4,456	1.763	12.62
Leachate 11	0.336	41.28	2,923	1.409	1.68	5.034	255.4	3,860	1.904	19.05
Leachate 12	nd	38.51	2,217	0.811	1.09	2.228	165.3	5,299	1.911	8.70
Leachate 13	0.267	42.18	1,998	0.745	1.27	0.445	146.6	2,914	2.018	24.76
Leachate 14	0.148	35.43	1,474	0.828	2.26	0.506	147.6	2,297	1.552	27.36
Leachate 15		32.78	1,430	0.936	1.35	1.564	90.1	1,829	1.357	26.81
Leachate 16		31.89	1,224	0.953	1.17	0.925	84.9	1,843	1.776	23.84
Leachate 17		29.09	312	nd	1.33	0.650	nd	781	0.558	8.23
Leachate 18		33.70	522	1.133	1.41	0.472	83.3	466	0.816	8.61
Leachate 19		31.26	643	0.752	0.94	nd	77.9	552	0.871	20.20
Leachate 20			872		0.85			857		19.83
Leachate 21			839		1.31			1,086		17.39
Leachate 22			850		1.19			1,226		19.66
Leachate 23			865		1.17			1,524		18.66
Leachate 24			1,288		1.20			1,101		19.09
Leachate 25			1,093		0.881			1,571		14.63
Leachate 26			931		0.910			1,623		13.36
Leachate 27			810		0.810			1,538		12.35
Leachate 28			839		0.880			1,307		13.35
Leachate 29			847		0.980			1,466		13.56
Leachate 30			784		0.850			1,466		13.15
Leachate 31			837		0.919			1,479		15.77
Leachate 32			1,083		1.162			1,390		16.62
Leachate 33			1,152		0.198			1,373		15.09
Leachate 34			1,045		0.930			1,240		15.63
Leachate 35			1,177		1.037			1,176		16.92
Leachate 36			1,403		0.698			1,080		12.33
Leachate 37			995		1.186			761		13.27
Leachate 38			971		0.822			871		14.76
Leachate 39			1,369		0.856			868		14.28
Leachate 40			1,263		nd			801		14.73
Leachate 41			1,276		nd			741		15.56
Leachate 42			1,452		0.707			766		16.51
Leachate 43			1,213		0.759			746		16.87
Leachate 44			1,034		0.770			689		15.54

¹ nd or blank = not determined

Table A13
Phosphate Runoff Concentrations After Each Rain Event (mg/L)

Rainfall Event	pH 7 lysimeters					pH 3 lysimeters				
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Runoff 1	0.77	36.2	126.0	2.70	8.78	0.73	54	245	1.54	11.63
Runoff 2	0.31	19.6	122.6	2.14	7.26	0.66	125	331	1.99	13.57
Runoff 3	75.65	30.4	130.0	2.60	7.27	4.13	147	735	1.45	10.16
Runoff 4	0.35	35.9	82.8	2.11	6.87	0.59	122	361	8.35	11.50
Runoff 5	0.67	35.9	49.9	1.39	3.71	0.37	200	772	2.88	11.29
Runoff 6	0.31	44.9	117.3	1.39	3.59	nd ¹	621	1697	42.1	234.9
Runoff 7	0.25	38.3	124.8	0.41	3.11	1.30	320	731	3.33	17.34
Runoff 8	0.26	33.6	287.3	0.92	2.28	1.28	322	751	6.60	45.37
Runoff 9	0.26	31.4	219.1	0.48	3.95	0.97	249	426	7.40	32.02
Runoff 10	1.44	27.5	235.0	0.32	1.71	0.80	397	381	5.31	35.07
Runoff 11	0.42	37.1	218.5	0.58	2.22	0.85	193	375	7.78	37.23
Runoff 12	0.28	28.8	246.7	0.39	1.65	0.71	205	372	4.92	31.84
Runoff 13	0.24	20.9	160.2	0.60	1.75	0.92	59	284	10.53	49.64
Runoff 14	nd	23.0	213.4	0.48	1.64	0.90	174	267	11.81	49.50
Runoff 15	nd	19.1	99.9	0.79	1.71	0.61	96	237	4.80	32.17
Runoff 16	0.62	15.7	120.3	1.17	0.80	0.64	76	190	8.00	36.05

¹ nd = no data

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14. ABSTRACT Because of the need for lead containment within small arms firing range (SAFR) impact areas, phosphate amendment has been proposed to reduce the release of lead via the surface and groundwater pathway. Both field and laboratory studies have evaluated the use of phosphates to stabilize lead in SAFR soils. The main goal of these studies was to determine the effectiveness of in situ phosphate treatment by demonstrating that phosphate addition to lead-contaminated soils resulted in soils that were stable to lead-leaching as measured by various standards. Because these studies were conducted using either large- or small-scale field demonstration projects or static laboratory procedures that were not capable of simulating conditions on actual ranges, their predictive value is limited. Prior to expending operational funds for large-scale soil amendment projects, further evaluation of the effectiveness of lead containment using phosphate amendment in a more realistic system is needed. This study evaluated the performance of two phosphate amendments in a more open dynamic system that simulated field conditions at SAFRs. The results of previous laboratory studies were extended by measuring and comparing losses of both soluble and insoluble lead in leachate and runoff from a treated and untreated SAFR soil using specially designed berm lysimeters. A rainfall simulation technique with the capability of increasing rainfall intensity and varying rainfall duration was developed to evaluate lead migration pathways at SAFRs.					
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